



Catalytic conversion of sugars and polysaccharides to glycols: A review

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ABSTRACT

Catalytic conversion of (ligno)cellulosic biomass at hydrothermal or pyrolysis conditions represent attractive approaches for the production of valuable oxygenated chemicals and platform molecules. Despite many efforts, there is still a knowledge gap in the fundamental phenomena occurring on the catalyst surface, considering the complexity of the reaction networks and catalyst behavior under reaction conditions. In this review, to gain a better understanding of the processes and for designing the most effective catalysts, the main reactions and possible products obtained from catalytic valorization of cellulose are discussed, focusing particularly on diols. The review illustrates how catalysts act for selective production of platform chemicals from cellulose and cellulose-derived sugars at both pyrolysis and hydrothermal conditions and systematically summarizes recent advancements of heterogeneous catalysts, with a view to structure-activity relationships for production of diols.

1. Introduction

To reduce the carbon footprint of the world by 2050, as stated in the Paris agreement, making carbon based materials, fuels and chemicals independent of fossil resources is a necessity. One way of doing this sustainably is by the “biorefinery” concept [1]. Lignocellulose, as the most abundant source of environmentally sustainable carbon, has the greatest potential to produce renewable fuels and chemicals, reducing the fossil-resource dependency of modern society [2]. Lignocellulosic biomass for production of fuels and chemicals is one of the hot topics of the 21st century, which is evidenced by the increasing number of publications during recent years (Fig. 1).

Lignocellulosic biomass mainly consists of cellulose (35–55%), hemicellulose (10–35%), and lignin (15–30%), having different composition, structure, building blocks and reactivity [3], as depicted in Fig. 2. Various methods such as gasification, (fast) pyrolysis, hydro-pyrolysis, hydrothermal liquefaction, etc. have been considered to convert lignocellulosic biomass mostly into renewable fuels due to their unselective nature [4–8]. Extensive research has been going on to diminish the high energy requirements of these methods as well as increase the yield of biofuels via developed processes and catalysts [7, 9–11]. In the case of chemicals, it has been reported that over 200 different molecules could be derived from lignocellulosic biomass by various treatment methods including pyrolysis and hydrothermal processes [12]. However, the complex chemical composition of

lignocellulosic biomass makes it more difficult to obtain specific target molecules in sufficiently high yields, compared to bio-fuel production in which a wide range of hydrocarbons are within the target range. As depicted in Fig. 2, cellulose is composed of only glucose units with a crystalline structure, while hemicellulose is composed of different five and six carbon sugar units with a random and amorphous structure [13]. Both cellulose and hemicellulose are polar biopolymers built from sugar monomers. In contrast, lignin is a complex, cross-linked, three-dimensional biopolymer of phenyl propane units with hydrophobic and aromatic properties [13]. Therefore, efficient fractionation of lignocellulosic biomass into its main components, i.e. cellulose, hemicellulose, and lignin, followed by selective transformation of each component to chemicals is attracting attention in order to obtain high quality products, increase flexibility of operation and reach full utilization of lignocellulosic biomass. Three fractionated streams could be upgraded into desired products under specific conditions such as temperature, pressure, hydrogen (H₂) partial pressure, residence time, catalyst, reactor configuration, etc. Treating individual components gives increased operational flexibility to produce a diverse spectrum of chemicals, such as sugars, alcohols, acids, furanic compounds, polyols, etc., with higher purity and quality (Fig. 2).

Since about 50% of the organic carbon in the biosphere is in the form of cellulose [13], the conversion of cellulose and cellulose-derived substances, i.e. mono- and di-saccharides, into value-added chemicals are of great importance in the context of biorefineries [21,22]. However, catalytic conversion of cellulose and cellulose-derived monomers into

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Nomenclature

AC	activated carbon	FDCA	2,5-furandicarboxylic acid
1,2 BDO	1,2-Butanediol	GA	glycolaldehyde
2,5-BHF	2,5-bis(hydroxymethyl)-furan	GlyA	glyceraldehyde
CNFs	carbon nanofibers	5-HMF	5-hydroxymethylfurfural
2,5-DFF	2,5-Diformylfuran	HMFA	5-hydroxymethyl-2-furancarboxylic acid
DHA	dihydroxyacetone	HMG	hydroxymethyl glyoxal
DHGly	dehydroglycerol (propene-1,2,3-triol)	HPA	hydroxy pyruvic acid
2,5-DMF	2,5-Dimethylfuran	LVG	levoglucosan
DMHF	dimethyl tetrahydrofuran	MEG	monoethylene glycol
3-DOG	3-Deoxyglucosone	MMF	methoxymethylfurfural
FCA	2-formyl-5-carboxyfuran	1,2-PDO	1,2-Propanediol
		PEF	polyethylene furanoate
		PVA	pyruvaldehyde

chemicals such as monoethylene glycol (MEG), 1,2-butanediol (1,2 BDO), hydroxymethylfurfural (5-HMF), methoxymethylfurfural (MMF), 2,5-furandicarboxylic acid (FDCA), etc. still encounter major challenges, such as poor selectivity, fast catalyst deactivation through coke formation, catalyst hydrothermal instability and sintering [23]. Solving the mentioned challenges and designing a well-performing catalyst is crucial to commercialize catalytic transformation of cellulose using a continuous reactor with stable productivity.

Designing the right catalyst with diverse functionality for production of chemicals from cellulose and cellulose-derived sugars determines the efficiency and profitability of a biorefinery. Despite many efforts, the research in this area is far from mature, so development of catalysts is needed to make biorefineries competitive with the petrochemical industries. Considering the complexity of the reaction networks and catalyst behavior under reaction conditions, there is a knowledge gap in the fundamental phenomena occurring on the catalyst surface. This motivates a systematic approach to study different catalysts through surface characterization and product distribution analysis. Enjamuri et al. [24] reviewed catalytic conversion of lignocellulosic biomass to ethylene glycol covering current ethylene glycol manufacturing processes, production of ethylene glycol from renewable resources and its production methodologies including biotechnological and chemocatalytic approaches. Manaenkov et al. [25] discussed trends in the development of catalysts for hydrolytic hydrogenation of cellulose with the formation of hexitols and glycols. In another work, Ma et al. [26]

considered transformation of cellulose and its derivatives to glycols, acids and nitrogen-containing chemicals, hemicellulose-derived furfural to jet fuel and lignin to aromatics using catalytic technologies. Yuan et al. [27] broadly reviewed approaches for conversion of lignocellulosic polysaccharides into chemicals including glucose, xylose, arabinose, 5-hydroxymethylfurfural, furfural, levulinic acid, lactic acid, sorbitol, mannitol, xylitol, 1,2-propylene glycol, ethylene glycol, ethanol, and gluconic acid. However, these reviews did not specifically investigate formation of C₂-C₃ oxygenates from glucose and polysaccharides. In another research, Sudarsanam et al. [28] comprehensively reviewed the role of supported MoO_x and WO_x solid acids and their catalytic effect on valorization of lignocellulosic biomass including cellulose, hemicellulose, and lignin. Although the above review highlighted the role of supported WO_x in biomass conversion, a comprehensive study focusing on the development of tungsten-containing catalysts for production of diol molecules from cellulose and hexose building blocks is not reported in the literature until now. Recently, Wu et al. [29] also broadly reviewed the conversion of lignocellulosic biomass, especially cellulose, into alcohols, acids, furan derivatives, ethylene glycol, and liquid hydrocarbon fuels over heterogeneous catalysts. However, this review did not thoroughly focus on C₂-C₃ diol formation.

Furthermore, Fitzgerald [30] discussed chemistry challenges for environmentally friendly and sustainable production of chemicals from biomass. Several studies evaluated the economic and environmental aspects of chemicals production from lignocellulosic biomass via

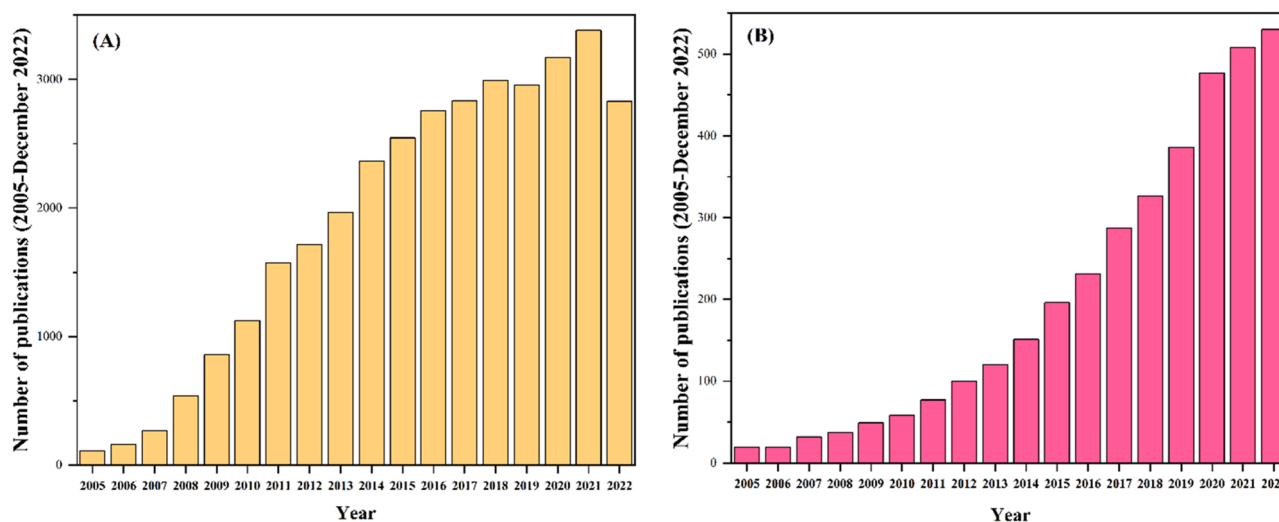


Fig. 1. Number of publications on production of biofuels (A) and chemicals (B) from lignocellulosic biomass per year.

Source: Web of Science [Graph A keywords: (bio-fuel/biofuel/transportation fuel) and (lignocellulose/ biomass/ cellulose/ hemicellulose/ lignin/ disaccharide/ sugars/ monosaccharides); Graph B keywords: (platform molecule/ fine molecules/ value-added molecules) and (lignocellulose/ biomass/ cellulose/ hemicellulose/ lignin/ disaccharide/ sugars/ monosaccharides)].

pyrolysis and hydrothermal processes [31–34]. Extensive economic and technical feasibility studies for glycols production from cellulose and cellulose-derived sugars is needed to guide future large-scale production as there are still challenges in these areas. However, this is not in the scope of the current study.

The current review illustrates how catalysts can enable the selective production of chemicals from cellulose and cellulose-derived sugars, with particular focus on tungsten-based catalysts due to their superior

activity for C–C bond cleavage (Fig. 3). Additionally, the perspectives of non-tungstic and tungsten-based, multifunctional catalysts are highlighted in order to selectively obtain value-added chemicals through different reaction pathways. Both catalytic hydrothermal and pyrolysis routes for diol production are discussed.

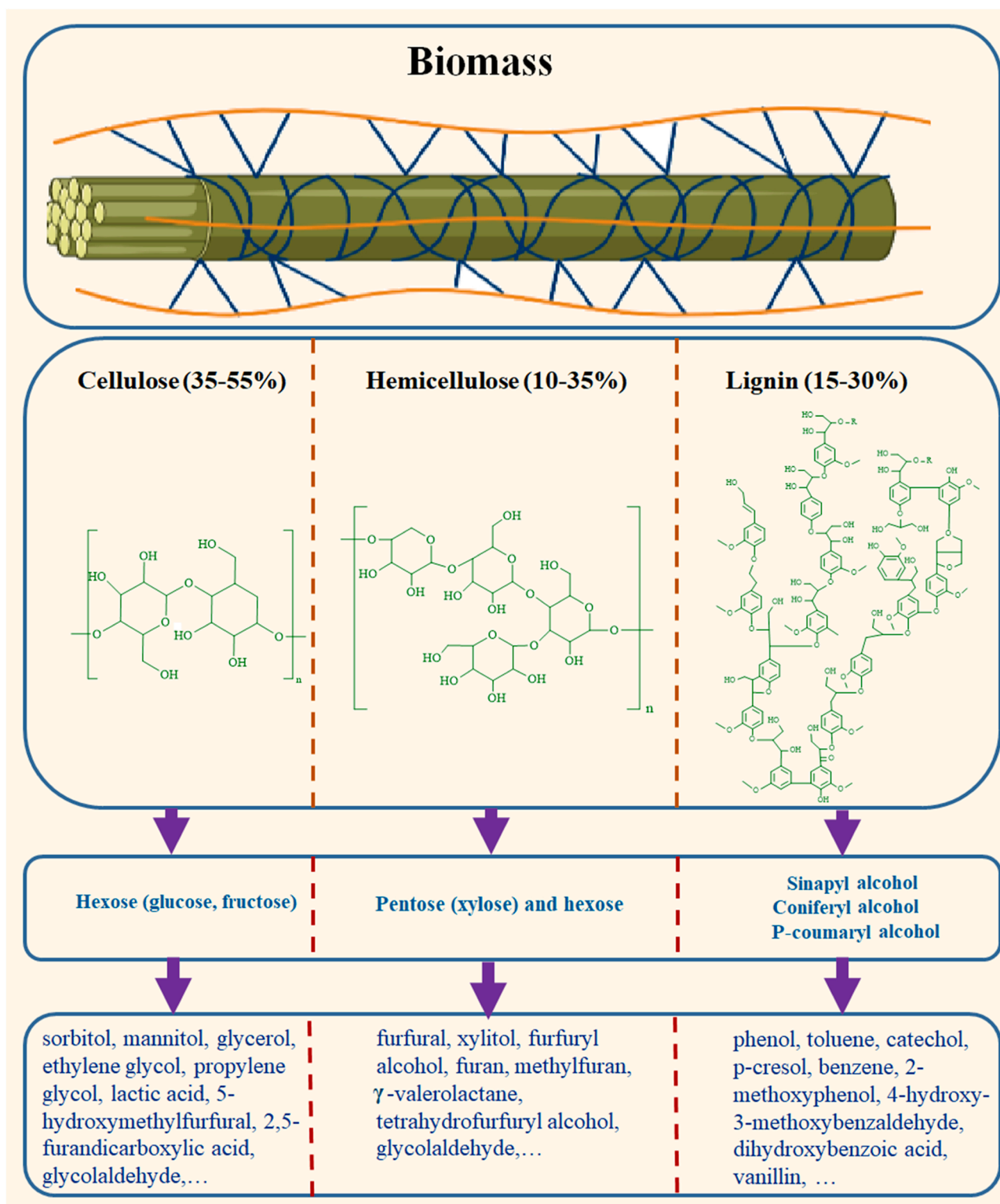


Fig. 2. Schematic of the components of lignocellulosic biomass and some of their associated platform molecules [14–20].

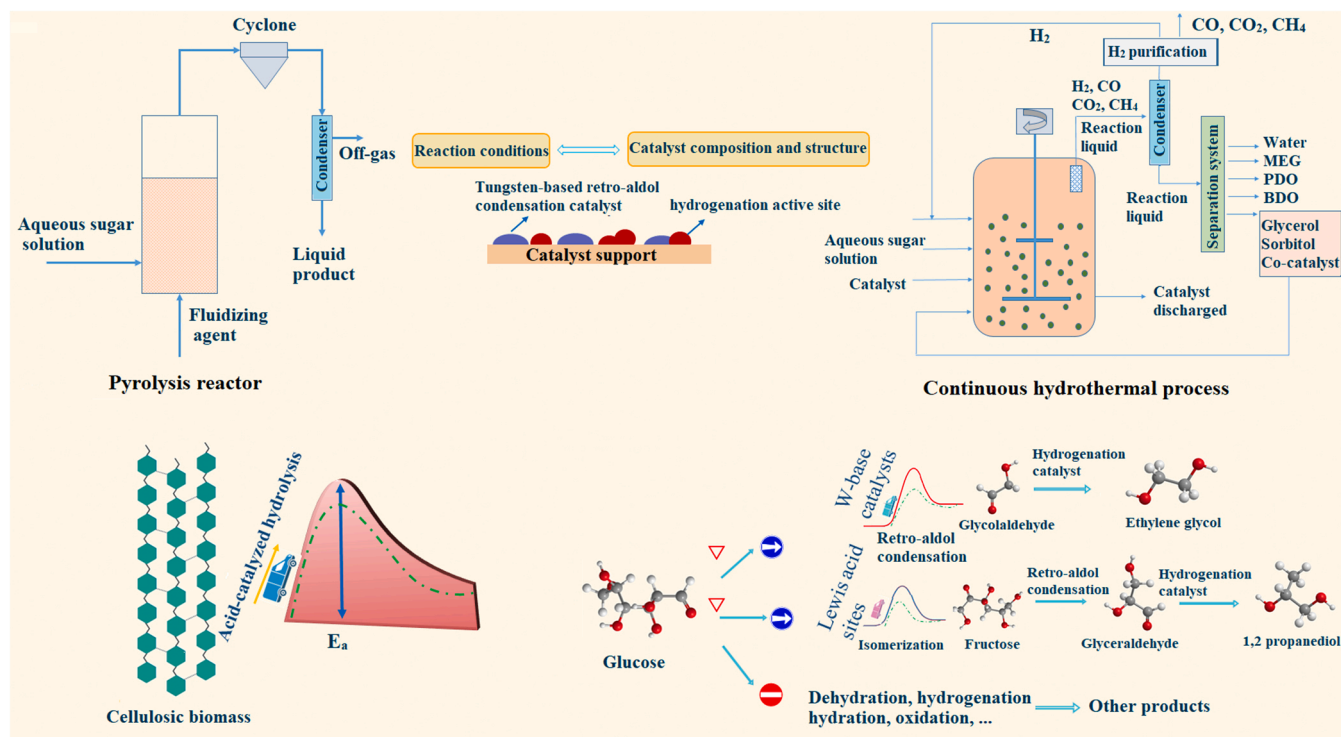


Fig. 3. Scope of the review: catalytic hydrothermal and (catalytic) pyrolysis processes of cellulose and cellulose-derived sugars.

2. Main reactions, reaction pathways and products

Many possible reactions including hydrolysis, dehydration, isomerization, Grob fragmentation, retro-aldol condensation, hydrogenation, dehydrogenation, hydrogenolysis, decarbonylation, retro-Claisen condensation, etc. can occur during catalytic conversion of cellulose, which makes a complex reaction network. Some of the main reactions are discussed in the following. Hydrolysis of cellulose into its glucose building blocks is an acid-catalyzed reaction, which is considered the first step of cellulose conversion into chemicals. Efficient hydrolysis of cellulose into glucose needs strong acidic conditions. However, for direct conversion of cellulose into chemicals, excessive acidity may have substantial adverse effects on subsequent reactions and reduce the reaction selectivity with respect to the target products by formation of humins [35]. On the other hand, in the case of heterogeneous catalysts, inefficient contact of the solid cellulose and the solid catalyst results in low yields. Therefore, hydrolysis of cellulose into sugars followed by transformation of the sugars into target molecules in separate reaction chambers is an attractive approach. In this regard, many research groups have been trying to fractionate lignocellulosic biomass and produce water-soluble carbohydrates, e.g. glucose, from non-food biomass resources instead of starch hydrolysis, which is currently the only commercialized method for sugar production for biorefinery purposes.

SEKAB, based in Sweden, developed a demonstration plant in which a sugar solution is produced from lignocellulosic biomass through their CelluAPP® technology applying steam acidic pretreatment and enzymatic hydrolysis [36]. The sugar then can be used in the production of different biochemicals and biofuels. Sweetwater Energy, based in the USA, fractionates lignocellulosic biomass and converts hemicellulose and cellulose into C5/C6 monomers using heat and dilute acid through their patented Sunburst™ technology [37,38]. Renmatix, USA, produces industrial C5/C6 sugars from a variety of biomass sources through a water-based technology called Plantrose™, in which supercritical water play a key role [39]. Bio-Sep Company, located in the UK, fractionates lignocellulosic biomass into cellulose, sugars, and lignin through their Bio-Sep technology using recoverable organic solvents and ultrasound

waves at moderate temperatures [40]. American Process inc. developed the AVAP® technology for producing low cost cellulosic sugars from non-food biomass through sulfur dioxide-ethanol-water fractionation [41]. Avantium, a Dutch Company, developed the Dawn technology™ to convert lignocellulosic biomass to high quality industrial glucose using concentrated hydrochloric acid at relatively mild conditions [42]. The plant-based sugars are then converted to MEG through RAY technology, a hydrothermal liquid phase process [43] and FDCA; finally, plastics such as PEF are produced combining MEG and FDCA, through the overall process called YXY® [44].

Using monosaccharides as feedstock for catalytic conversion processes could produce platform molecules in high yields and with fewer separation and purification steps compared to when starting from cellulose. To give an overview, some of the possible platform molecules that could be derived from glucose via different reaction pathways are illustrated in Fig. 4. A wide range of biomass-based chemicals and platform molecules such as MEG, 1,2 BDO, 5-HMF, MMF, FDCA, sorbitol, mannitol, erythritol, levulinic acid, lactic acid, glycerol, methyl lactate, alkyl lactate, methyl levulinate, gluconic acid, glucaric acid, etc. may be produced. The possibility to produce a wide range of products from monosaccharides confirms the tremendous potential for industries to replace oil-based chemicals and fuels. However, uncontrolled reaction conditions result in undesired products, a wide product distribution as well as gaseous products and coke formation. Depending on the type of solvent, e.g. water, alcohol, ionic solvent, etc., the presence of reactive gases, e.g. H₂ and O₂, the type and nature of catalyst, and presence of salts some of the reactions will be dominant. Fig. 4 summarizes the reactions occurring with water as solvent.

These reactions include isomerization, retro-aldol condensation, oxidation, dehydrogenation, dehydration, rehydration, and hydrodeoxygenation and may occur at both hydrothermal and pyrolysis conditions. However, for oxidation and hydrogenation reactions the presence of an oxidation or hydrogenation agent is required.

For C₂-C₃ glycols production, monosaccharides can undergo the primary reactions glucose to fructose isomerization, dehydration, retro-aldol condensation, and hydrogenation when hydrogen is present under



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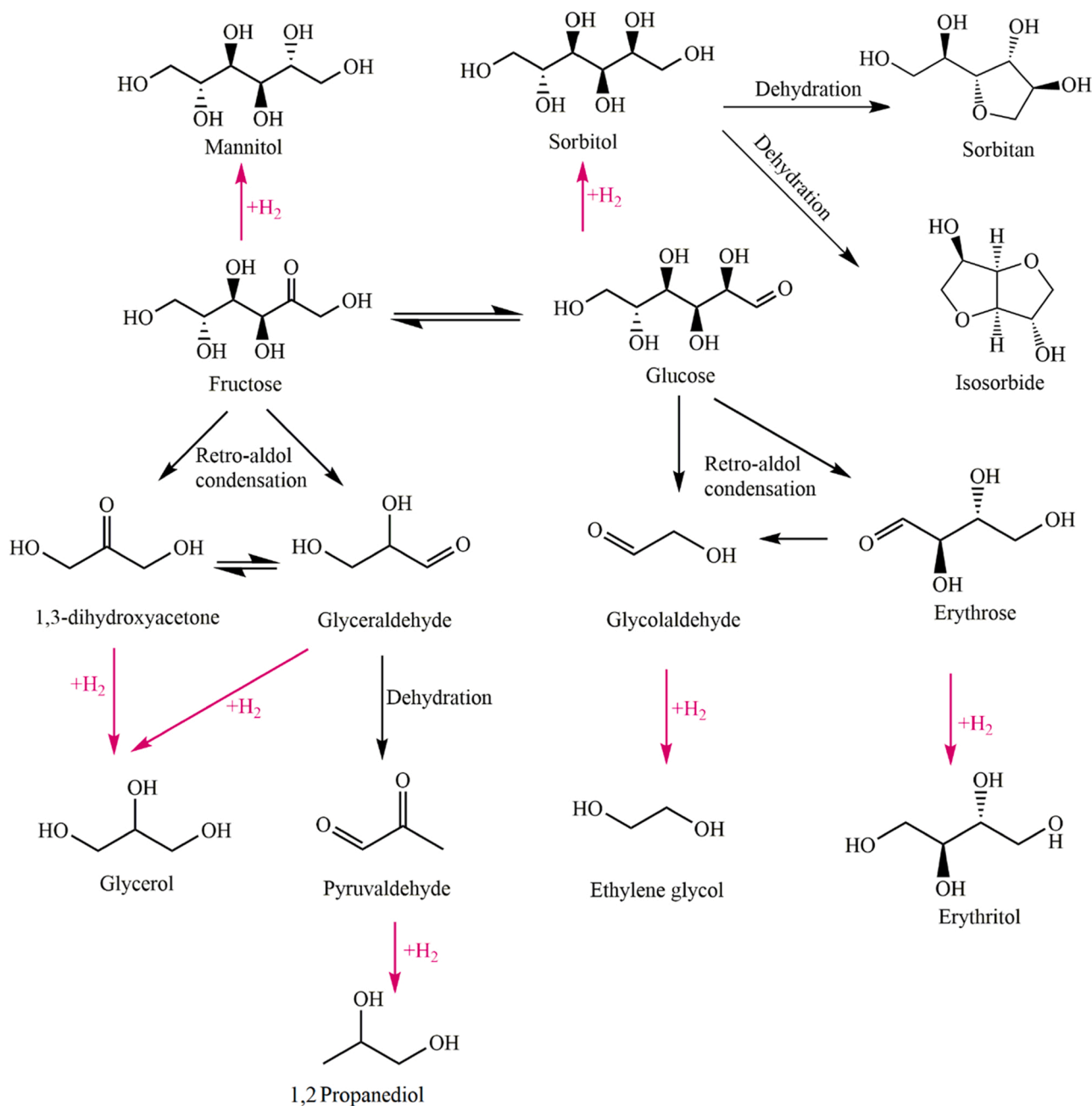


Fig. 5. Hydrogenation of some monosaccharides and derivatives in the reaction media in presence of hydrogen and a hydrogenation active catalyst [86–89].

~65 kJ/mol [87]. Sorbitol could undergo consecutive dehydration to produce sorbitan and isosorbide in the presence of solid acid catalysts [48]. In parallel, hydrogenation of fructose to mannitol with similar activation energy and hydrogenation of glucose derivatives such as glycolaldehyde (GA) to MEG with an activation energy of ~37 kJ/mol could happen [87,88].

Retro-aldol condensation of the sugars is the dominant reaction for C–C bond cleavage that can be catalyzed by base sites or transition metal sites [77]. Generally, the activation energies for the retro-aldol condensation of sugars (~160 kJ/mol) are higher than that of sugar isomerization (~140 kJ/mol) and sugar hydrogenation (~35–65 kJ/mol) [75,87,90,91]. This indicates that the retro-aldol reaction is much more sensitive to the reaction temperature compared to the sugar hydrogenation and isomerization reactions. Therefore, isomerization and hydrogenation of sugars dominate over retro-aldol condensation at relatively low temperatures, i.e. < 200 °C [92]. Thus,

fast heating to the required temperature is needed to target the retro-aldol reaction leading to production of light oxygenates as dominant products, circumventing undesired side reactions, while slow heating rates may result in production of dehydration products such as anhydrosugars, particularly levoglucosan [93]. Both basic and Lewis acid sites could promote the isomerization, retro-aldol condensation, dehydration and polymerization reactions [94]. Tuning the catalyst activity and characteristics, including the strengths of acidic and basic sites, substantially alter the reaction selectivity towards different molecules [95].

Many other products can be produced if water is replaced with alcohols as solvent [96]. Methyl lactate, as an example, is one of the platform molecules that could be derived from lignocellulosic biomass using methanol as reaction medium [97–99]. A lot of research in methyl lactate production from both cellulose and cellulose-derived sugars has been conducted to promote the process using different kinds of

heterogeneous catalysts [64,100–104].

Most of the reactions presented in Fig. 4 could potentially occur in the reaction chamber in parallel or as consecutive reactions with water as solvent. For instance, for lactic acid production, tandem reactions including, glucose to fructose isomerization, retro-aldol condensation of fructose to glyceraldehyde, dehydration of glyceraldehyde to pyruvaldehyde, and finally pyruvaldehyde to lactic acid are involved [105–108]. The produced lactic acid could be used in chemical, pharmaceutical, and food industries [27]. To promote the desired pathway and obtain a high selectivity with respect to the target molecule, one must control the major reaction steps in the reaction network by manipulating the operating conditions and designing proper catalysts with tuned characteristics. However, this could be challenged by the fact that the energy barrier for some of the reactions are in the same range. To increase the selectivity of the desired main reaction product, thermodynamics and kinetics have to be taken into consideration to avoid/minimize unwanted side reactions. Here reactor configuration and product separation strategies could also have a transformative effect on the purity of individual products. In the following the production of diols and furanics, as very important platform molecules in bio-refineries, are discussed to highlight the importance of reaction pathways.

Diols such as MEG and 1,2-PDO are among the high-value chemicals widely used for synthesis of polyesters, antifreeze, and chemicals. The market for these diols is expected to grow as the global demand for clothes, unsaturated resin materials, etc. is growing [12]. Recently, with the development of plant-based polymers, e.g. polyethylene furanoate (PEF), the production of diols using renewable biomass is gaining more attention. Generally, high yield and selectivity of diol production from lignocellulosic biomass and sugars is challenging due to the complex reaction routes and the many intermediate and byproducts [109]. To produce MEG from glucose, the retro-aldol condensation reaction needs to be the dominating pathway in which GA and erythrose are formed as a first step (Figs. 4 and 5) [45,89,110]. Erythrose undergoes further retro-aldol condensation to form two further GA molecules in the absence or presence of a catalyst [89,111]. GA could be hydrogenated to MEG either in the same reaction media [43] or in a subsequent hydrogenation reactor using an active hydrogenation catalyst [112]. So, in order to increase the selectivity with respect to MEG, as an example, one should increase the selectivity to retro-aldol condensation and hydrogenation of the formed GA, while suppressing other undesired reactions, e.g. isomerization of glucose to fructose, dehydration, hydrogenation of glucose to sorbitol, etc., by designing proper catalysts and optimizing operating conditions. For example, at very short residence times, fast pyrolysis of an aqueous glucose solution sprayed into a fluidized bed reactor around 500 °C minimizes isomerization of glucose into fructose [89,110,111], resulting in very high (>70%) selectivity towards GA. This confirms the effect of heating rate, residence time, and reactor configuration on product distribution.

One-pot retro-aldol condensation and hydrogenation may be attractive due to the fact that MEG is relatively stable under the reaction conditions [71], compared to GA, which is prone to subsequent polymerization reactions. However, the presence of H₂ in a one-pot process may activate hydrogenation of sugars before the retro-aldol reaction, which would lead to lower selectivity with respect to MEG. The hydrogenated sugars, e.g. sorbitol, undergo hydrogenolysis reactions to produce more stable products, ending with 1,2-PDO. The design of a one- or two-step configuration is a function of the dominating reaction pathways, catalyst properties, solvent type, additives, and operating conditions, i.e. feed flowrate, residence time, temperature, pressure, etc. For 1,2-PDO production, isomerization of glucose to fructose is also a possibility prior to retro-aldol condensation, as shown in Fig. 4.

5-HMF, FDCA and 2,5-dimethylfuran (2,5-DMF) are the main representatives of the furanics (furan derivatives) family, which could be derived from glucose through selective isomerization and subsequent dehydration, hydrogenation, oxidation and hydrodeoxygenation

(Fig. 4). Furanics have been identified as high potential renewable intermediate chemicals for bio-polymers production. For FDCA production, it is crucial to increase the isomerization of glucose to fructose, to avoid glucose dehydration, and the following dehydration reaction of fructose should be dominant. FDCA could be polymerized in the presence of MEG to form PEF, which is a 100% recyclable plant-based polymer with superior properties, e.g. mechanical strength, gas barrier property against O₂/CO₂ diffusion, compared to conventional PET plastics [113]. As it can be seen in Fig. 4, 5-HMF can be produced from glucose through either consecutive dehydration or through an intermediate isomerization step to fructose and subsequent dehydration of two water molecules from fructose into 5-HMF [49,54,57]. However, fructose is much more reactive than glucose for dehydration into 5-HMF, therefore the isomerization-dehydration pathway is preferred [114]. Other reactions, e.g. retro-aldol condensation, compete with the dehydration reaction, especially at elevated temperatures, > 350 °C [82,115,116], decreasing 5-HMF selectivity. This is due to the fact that monosaccharides are prone to ring-opening in aqueous solutions, which could be followed by retro-aldol condensation, resulting in less anhydrosugars and subsequently lower 5-HMF selectivity. Therefore, one may prefer to use cellulose, which cannot ring-open, as the starting material for 5-HMF production. However, using cellulose as starting material challenges the yield, due to the inefficient contact of solid cellulose with heterogeneous catalysts. In this regard, ring-locking is a promising method that recently has been utilized to restrain sugars from ring-opening [117]. In this method, the OH group at the anomeric carbon of glucose is substituted with an alkoxy or phenoxy group, which make it difficult to open the ring. Ring-locked sugar dehydrates to anhydrosugars (e.g. levoglucosan) and 5-HMF under pyrolysis conditions with minimum undesired retro-aldol condensation. Subsequently, 5-HMF could also undergo rehydration to produce levulinic acid (LA), which is an important platform molecule that could be used to synthesize biofuels, resins, pharmaceuticals, herbicides, polymers, flavouring agents, etc. [66,118].

In order to produce a specific product, certain reactions should be promoted and others inhibited, highlighting the crucial role of catalysts capable of catalyzing the desired reactions, in order to maximize the selectivity with respect to the target product(s). Design and tuning of multi-component catalysts for polyol production is discussed in the next section.

3. Light oxygenates: C2-C3 polyols

This section focuses on the production of C2-C3 diols, i.e., MEG and 1,2-PDO, two valuable, high-volume chemicals that can be produced from cellulose and its building block, glucose. As depicted in Fig. 6, two promising routes, i.e. hydrous pyrolysis and catalytic hydrothermal process, are widely researched for selective production of MEG. Production of 1,2-PDO is targeted mainly through the catalytic hydrothermal route. In the following sub-sections, first pyrolysis of both cellulose and glucose with the capability of MEG production is discussed (Section 3.1), then catalytic hydrothermal routes with focus on tungsten-based catalysts for production of MEG, and 1,2-PDO are evaluated (Section 3.2).

3.1. Pyrolysis route

Pyrolysis processes, which operate in an oxygen-free environment at 400–600 °C, have been extensively applied for producing pyrolytic bio-oil from lignocellulosic biomass [9,11,119,120]. This process has also been considered to selectively produce bio-based platform molecules. Pyrolysis/fast pyrolysis of cellulose in (micro) pyrolyzers give numerous volatile species, e.g. levoglucosan, 1,6-anhydroglucofuranose, dianhydroglucopyranose, furfural, 5-HMF, furan-3-methanol, 2,5-dimethylfuran, methylglyoxal, hydroxyacetone, glycolaldehyde, formic acid, and formaldehyde, due to the thousands of elementary reactions [116,

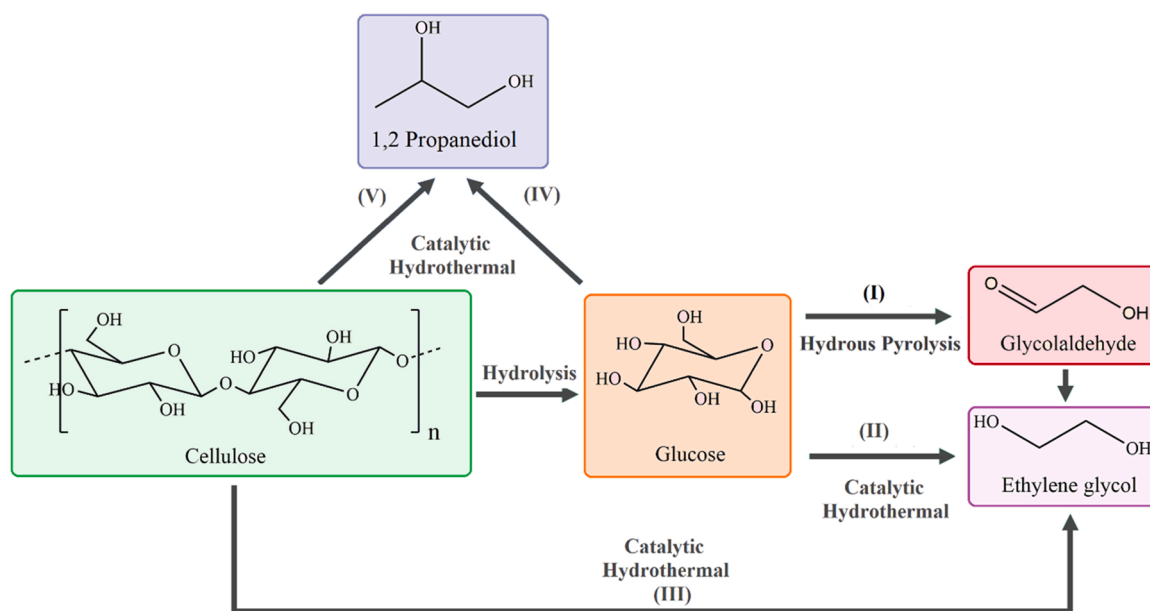


Fig. 6. Overview of monoethylene glycol and 1,2 propanediol from cellulose and glucose.

[121,122]. The selectivity of cellulose pyrolysis towards specific molecules is therefore not high enough to be industrially relevant. The products of cellulose pyrolysis inside a micro-pyrolyzer are classified as anhydrosugars, light oxygenates, furan compounds, char, and permanent gases. The yields of three dominant components, i.e. levoglucosan, glycolaldehyde, and 5-HMF, as representatives of anhydrosugars, light oxygenates, and furans respectively are shown in Fig. 7 [75,116,121,123–126]. The yields reach constant values within 2.5–3 s of pyrolysis time [123]. The yield of permanent gases, i.e. CO and CO₂, increased monotonically, while char formation decreased as the temperature increased. Above 600 °C, gaseous products started to be dominant with CO as the main gas due to the presence of abundant -HCOH functionalities in cellulose [127]. The total yield of anhydrosugars and furans first increases with increasing temperature to 400–450 °C and then decreases due to secondary reactions of the formed species. Specifically, the yield of levoglucosan, the most dominant anhydrosugar, monotonically decrease as pyrolysis temperature increased from 350° to 650°C. However, the yield strongly depends on specific operating conditions such as heating rate and sample size. The yields of 5-HMF, did not exceed 3 wt% during cellulose pyrolysis at different temperatures [75,116,121,123–125]. The total yield of light oxygenates, including hydroxyacetone, methyl glyoxal, GA, formic acid, and formaldehyde, increase gradually with increasing temperature. However, the yields of the individual light oxygenates follow different trends. For example, in some cases the yield of GA first increased then decreased as pyrolysis temperature increased. This is due to the fact that formation of GA competes with reactions with higher activation energy in which further degraded molecules, e.g. formaldehyde and acetaldehyde, are produced [128].

Much research has also been devoted to pyrolysis of solid glucose using micro pyrolyzer reactors [75,82,126,129–133]. For comparison, the distribution of the main product groups from glucose and cellulose fast pyrolysis is depicted in Fig. 8, where most of the substrate was converted into anhydrosugars, furans, light oxygenates, char and permanent gases. In addition, water was also produced as a result of dehydration reactions. Similar to cellulose, the pyrolysis of glucose resulted in a wide product distribution with low yields for the dominant products, i.e. levoglucosan (5–15 wt%), GA (5–20 wt%), and 5-HMF (3–12 wt%) [75,82,126,131,132]. Furthermore, as expected, MEG and 1,2-PDO were not among the products due to the absence of a hydrogen source and hydrogenation active catalyst.

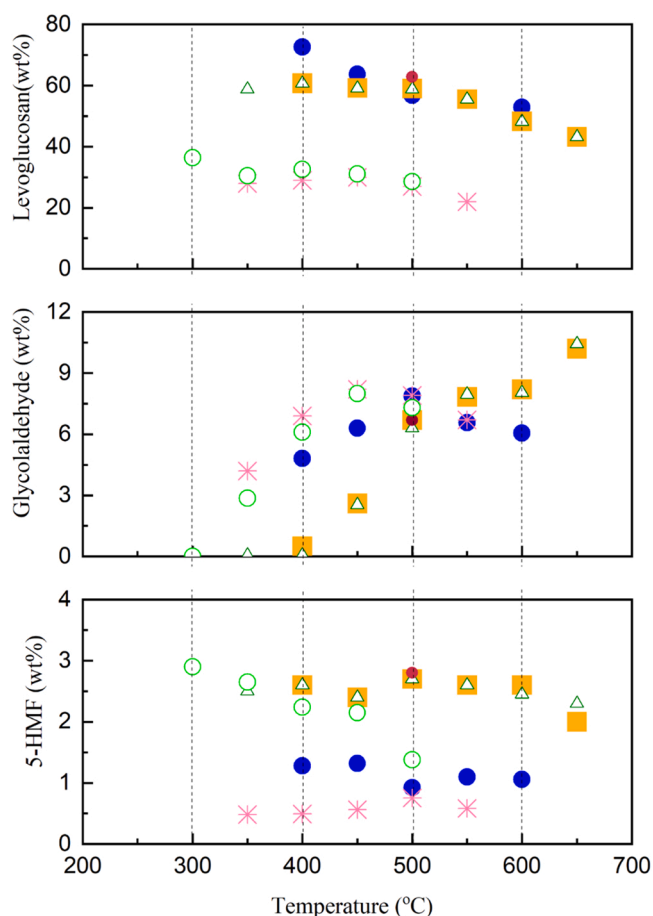


Fig. 7. Yields (in weight percent) of levoglucosan, glycolaldehyde, and 5-HMF from fast pyrolysis of cellulose in a micro-pyrolyzer at temperatures ranging from 300° to 650°C (○[121]; ●[75]; ■[123]; ●[124]; △[125]; * [116]).

The use of an aqueous solution of sugars at pyrolysis condition, i.e. hydrous pyrolysis, altered the product distribution significantly with substantially improved GA selectivity in comparison with that of solid

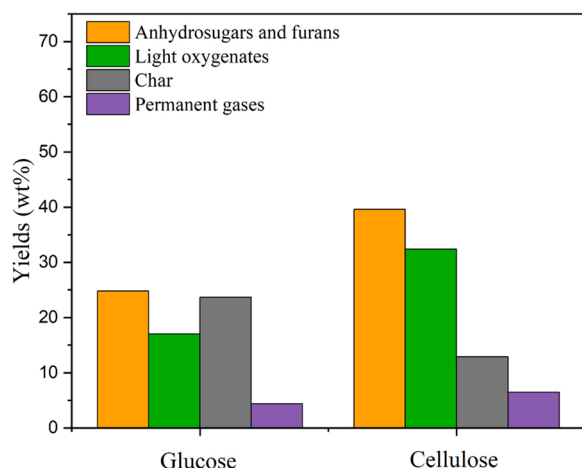


Fig. 8. Yields of the main product groups from pyrolysis of cellulose and glucose in a thin-film micro pyrolyzer at 500 °C [131].

sugar or cellulose pyrolysis in micro pyrolyzers [89,111,134]. The presence of water facilitated pericyclic fragmentation reactions of carbohydrates and minimized reactions such as formation of cyclic anhydrosugars, char and permanent gases [111]. Hydrous pyrolysis is typically performed in a fluidized bed reactor where an aqueous sugar solution is sprayed over the bed material, e.g. fine glass beads, with an optimum temperature in the range of 500–600 °C and gas residence time of ~1 s [110]. Near complete conversion of glucose with GA selectivity above 70 wt% was achieved in hydrous pyrolysis using a fluidized bed reactor at temperatures in the range of 500–550 °C [89,111]. Pyruvaldehyde (9 wt%), formaldehyde (7 wt%), glyoxal (2 wt%), acetol (2 wt%), and acetic acid (1 wt%) were the main by-products. Trace amounts of anhydrosugars (< 1 wt%) were also formed [89]. GA can be further converted into a range of chemicals such as MEG [135], ethylene diamines [136], and glycolic acid [137] through catalytic hydrogenation, reductive amination, and oxidation, respectively. The companies Topsoe A/S and Sustainea Bioglycols are developing a two-step process in which glucose is cracked to GA in a hydrous pyrolysis fluidized bed reactor followed by hydrogenation to MEG in a separate reactor [112]. The type of bed material in the fluidized bed play an important role affecting the yield of GA [135,138]. Bed materials, such as soda-lime glass, recycled glass, beach sand, mullite, and alumina, were used in the fast pyrolysis reactor. Soda-lime glass, resulted in minimized undesired reactions and highest yield of GA of 74%. [89,135]. Low residence time (< 2 s) and relatively high temperature (>500 °C) favored the highly endothermic retro-aldol reactions with high energy barrier to occur to a higher extent than competing reactions. Therefore, hydrous pyrolysis of glucose could be a promising approach to produce GA, as the immediate product of glucose retro-aldol condensation, and subsequently MEG through hydrogenation. An active catalyst which is capable of selectively catalyzing retro-aldol reactions and has high mechanical strength for application in a fluidized bed reactor could help this reaction to occur more efficiently, which would increase its economic competitiveness.

The Archer Daniels Midland Company recently filed a patent describing a fluidized bed system using various catalytic bed materials for hydrous pyrolysis of glucose for GA production [139]. Metal oxides from group 4, 5, and 6 of the periodic table were coated on different support materials, e.g. glass and ceramics, and the process performance was significantly improved in comparison with that of the bare support. The GA yield reached up to 85% using molybdenum oxide-coated glass beads at 525 °C with N₂ as fluidizing agent.

In conclusion, pyrolysis of cellulose and cellulose derived sugars at dry condition lead to a wide product distribution while hydrous pyrolysis of glucose could give high yields of small oxygenates, mainly

glycolaldehyde as a valuable platform molecule. However, this method is applicable only for sugars that can be dissolved in water. Furthermore, MEG and 1,2-PDO production require an additional hydrogenation process. Research on this process is ongoing to further increase overall economic efficiency.

3.2. Hydrothermal route: heterogeneous catalysts

As demonstrated in the previous sections the four main reactions isomerization, dehydration, retro-aldol condensation, and hydrogenation are actively competing with each other when producing C2-C3 diols from sugars.

However, with cellulose as feedstock, hydrolysis of cellulose into monomers must occur prior to the above-mentioned reactions. The resulting sugars are then transformed into valuable platform molecules in the same reaction medium or in a secondary reaction vessel. One-pot conversion of cellulose into MEG, as an example, passes through three consecutive reactions [140]. Firstly, cellulose is hydrolyzed into glucose, secondly, glucose is converted into GA by retro-aldol condensation, and finally, GA is hydrogenated to MEG. 1,2-PDO could also be produced through the isomerization of glucose to fructose prior to retro-aldol condensation and hydrogenation. Therefore, the ideal catalyst of this reaction must have ability of solvent acidification for cellulose hydrolysis and multiple active sites, including the retro-aldol condensation and the hydrogenation of GA to MEG. The selectivity of the overall reaction is determined by the interplay between these reactions. To intensify the desired reactions in a balanced way and obtain a high yield of the target molecule, design and application of a multi-functional catalyst is unavoidable. This is reviewed in the following subsections.

Tungsten containing catalysts were found to be among the most effective for the crucial retro-aldol condensation reaction in diol production from saccharides. Due to the importance of tungsten oxide, the following subsections are initiated with tungsten containing catalysts. Their application and effect in cellulose- and glucose-based hydrothermal processes are discussed. The role of different supports and their interaction with tungsten oxide is reviewed. The discussion is continued by reviewing other heterogeneous, non-tungstic catalysts.

3.2.1. Tungsten-containing catalysts

As depicted in Fig. 5, the retro-aldol reaction is the key reaction for production of both MEG and 1,2-PDO. It has been reported that some transition metals forming acidic oxides, mainly from groups 3–6 and 14 of the periodic table, are catalysts for the retro-aldol condensation reaction [109]. Among them, elements of group 6 of the periodic table, i.e. W, Mo and Cr, have been shown to be the most effective catalysts [141–143]. Tungsten-based catalysts are known as efficient solid acid catalysts in many applications, including isomerization of alkenes, selective oxidation of unsaturated compounds, selective reduction of nitric oxide, dehydrogenation of alcohols, hydrodesulfurization and hydrocracking of heavy fractions in the petroleum chemistry [144,145]. Many studies about synthesis and application of tungsten containing catalysts for one-pot conversion of both cellulose and glucose into polyols have been published [35,146–171]. In the following W-based catalytic processes are divided into cellulose-based and glucose-based processes.

3.2.1.1. Cellulose-based processes - multi-functional catalysts. Particularly bi-functional catalysts, with the ability of catalyzing hydrolysis, isomerization, retro-aldol condensation, and hydrogenation have been shown to be active in hydrothermal conversion of cellulose into glycols [35,146–149]. As can be seen in Table 1, all experiments were performed under H₂ pressures of 40–70 bar, and moderate temperatures (180–260 °C) with reaction times of 1–3 h in batch reactors. Cellulose could be hydrolyzed to sugars, catalyzed by H⁺ ions generated at high temperature (>200 °C) [147]. Both noble and non-noble metals have been used as hydrogenation functionality and various tungsten species,

Table 1

Hydrothermal conversion of cellulose into glycols in the presence of bi-functional catalysts and hydrogen atmosphere.

Entry	Cellulose concentration in water (wt %)	Catalyst	Reaction parameters			Conversion (%)	Yield ^a (%)		Ref.
			T (°C)	P _{H2} (atm)	Time (h)		MEG	1,2 PDO	
1	2.5	1 wt% Ru/WO ₃	180	40	2	5.2	3.8	2.5	[146] ^a
			200			65.8	16.4	7.8	
			220			84.2	49.2	3.7	
			240			100	76.3	4.3	
			260			100	72.6	3.6	
2	0.75	WO ₃ + Ru/AC	225	45	2	39.7	11.7	0.0	[35] ^b
		<i>b</i> -WO ₃ + Ru/AC			2	75	37.9	1.65	
		<i>b</i> -WO ₃ + Ru/AC			1	62.3	37.9	1.7	
		<i>b</i> -NbW ₅ + Ru/AC			2	80.1	35.5	2.6	
		<i>b</i> -TiW ₅ + Ru/AC			2	95.6	32.8	5.1	
		<i>m</i> -WO ₃ + Ru/AC			2	82.1	40.9	1.9	
		<i>m</i> -WO ₃ + Ru/AC			1	66.7	33.1	3.7	
		<i>m</i> -NbW ₅ + Ru/AC			2	83.5	42.4	3.1	
		<i>m</i> -NbW ₅ + Ru/AC			1	64	36.3	2.1	
		<i>m</i> -TiW ₅ + Ru/AC			1	70.3	34.5	4.8	
		<i>m</i> -VW ₅ + Ru/AC			1	57.2	22.1	1.0	
		<i>m</i> -ZrW ₅ + Ru/AC			1	74.3	33.4	3.1	
		30%WO ₃ /AC	245		2	78	4.0	1.0	
		30%Cu/AC				99	1.0	5.0	
3	1	10%Ni/AC				91	21.0	11.0	[148] ^c
		30 wt%Cu–30 wt%WO _x /AC				100	3.0	15.0	
		30 wt%Cu–30 wt%WO _x –10 wt%Ni/AC				100	58.0	7.0	
		30 wt%Cu–30 wt%WO _x /AC + Ni/AC				100	70.5	4.5	
4	5	2 wt%Ru/Zr–W	220	65	3	90.5	25.5	4.8	[149] ^c
		3 wt%Ru/Zr–W				81.9	30.0	4.2	
		4.5 wt%Ru/Zr–W				72.2	31.9	4.5	
6	2	Fe ₃ O ₄ @SiO ₂ /10%Ru–20%WO _x	245	50	2	96.8	19.7	31.4	[172] ^d
7	1	Ni–N–C–600 ^e + WO ₃	245	60	1.75	100	36.8	4.3	[173] ^d
8	1	Co@C + WO ₃	240	30	3	100	67.3	3.7	[174] ^c
5	1	5 wt% Ru/C + WO ₃	245	50	2	100	58.4	4.3	[175] ^c

^a Calculated as : Yield (%) = $\frac{\text{carbon atoms of polyol in the products}}{\text{carbon atoms of converted cellulose}} \times 100$

^b Calculated as: Yield (%) = Selectivity of polyol \times cellulose conversion

^c Calculated as : Yield (%) = $\frac{\text{carbon atoms of polyol in the products}}{\text{carbon atoms of cellulose charge into the reactor}} \times 100$

^d Calculated as : Yield (%) = $\frac{\text{weight of product}}{\text{weight of cellulose charge into the reactor}} \times 100$

^e Calcination temperature of 600 °C

particularly WO₃ and W containing mixed oxides, as the retro-aldol functionality of the catalyst.

Li et al. synthesized Ru/WO₃ with (0–3 wt% Ru) and used it for conversion of cellulose to MEG under hydrothermal conditions (P_{H2}=10–50 bar, T = 180–260 °C) [146]. The highest MEG yield, 76.3%, was achieved in the presence of 1 wt% Ru loaded on WO₃ nanosheets at optimized conditions (Fig. 9). 1 wt% of other hydrogenation active metals, i.e., Ni, Ir, Rh, Pt, and Pd on WO₃ showed lower yields of glycols (Fig. 9). Li et al. showed that the presence of Ru particles in the vicinity of WO₃ resulted in higher levels of W⁵⁺ species on the catalyst due to hydrogen spillover under the reducing conditions. W⁵⁺ species acted as active Lewis base sites and catalyzed the glucose retro-aldol condensation.

Wiesfeld et al. [35] investigated the effect of bulk tungsten oxide (*b*-WO₃) and mesoporous tungsten oxide (*m*-WO₃) on depolymerization of cellulose to glucose and retro-aldol condensation of glucose to C₂ aldehydes. The intermediate C₂ aldehyde further converted to MEG using carbon supported Ru as hydrogenation function in the same reaction medium. The cellulose conversion increased with increasing reaction time, while the selectivity to MEG decreased. After 2 h reaction (225 °C, 45 atm H₂), the yield of MEG in the presence of *b*-WO₃ and *m*-WO₃ reached 37.9% and 40.9%, respectively, which was higher than that of monoclinic WO₃ with 11.7% MEG yield. This was attributed to the increased surface area of *b*-WO₃ and *m*-WO₃ compared to monoclinic

WO₃. Doping *b*-WO₃ and *m*-WO₃ with transition metals, such as Ti, V, Zr, and Nb, enhanced the rate of cellulose depolymerization to glucose through higher Brønsted acidity that probably leads to higher acidity of the liquid. However, the higher acidity of these mixed oxides resulted in a higher rate of humin formation instead of retro-aldol condensation, so the overall yield of MEG did not improve substantially.

Chu et al. [148] revealed the superior impact of lower valence state W (V or IV) to high valence state W(VI) on retro-aldol condensation. They modified surface oxygen vacancies of WO₃ through forming CuWO₄ with varying Cu loading. Cu⁰ and oxygen deficient WO_x (2 < x < 3) species were formed by reduction of CuWO₄. A 30 wt% Cu–30 wt% WO_x/AC catalyst together with Ni/AC, could efficiently catalyze cellulose conversion into MEG with a yield of 70.5% (Table 1, entry 3), which was higher than that of the individual Ni/AC, Cu/AC and WO₃/AC catalysts. They demonstrated that the presence of Cu in the catalyst structure led to a higher ratio of low to high valence state W. With 30 wt% Cu loading on WO₃, the W⁵⁺/W⁶⁺ ratio reached 25%. Dissociated H on Cu⁰, partially reduced W leading to oxygen vacancies, which are active for the retro-aldol reaction through adsorbing C₆ sugars. It was proposed that Cu⁰ species did not directly catalyze retro-aldol reaction and its role was to mainly reduce the tungsten oxide through hydrogen spillover. Subsequently, Ni supported on activated carbon hydrogenated the formed intermediate GA into MEG and avoided coking since the GA is prone to polymerization and coke formation.

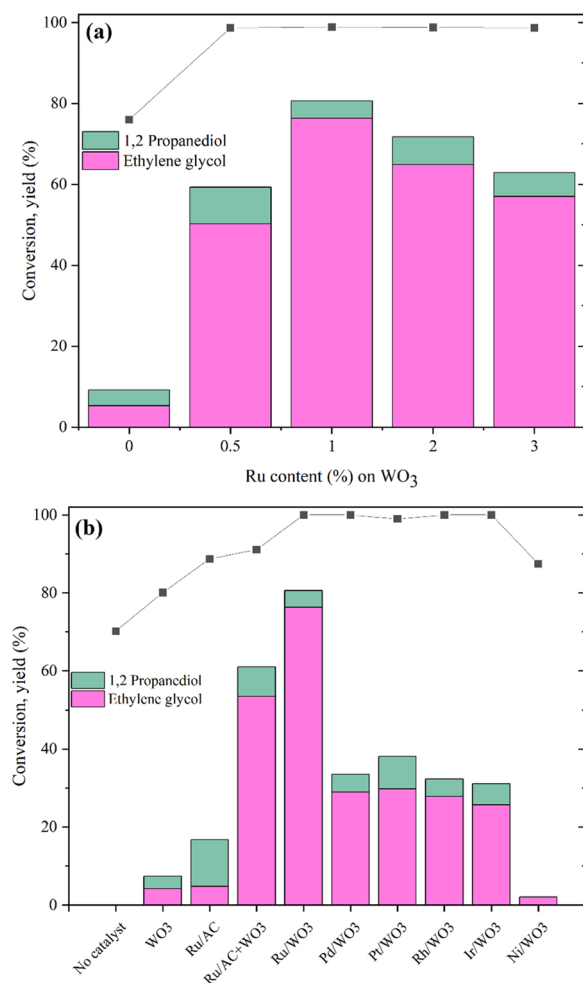


Fig. 9. Total cellulose conversion, ethylene glycol and 1,2 propanediol yields (a) at various Ru content and (b) different catalysts (1 wt%) after 2 h reaction at 240 °C and 40 bar H₂ pressure [146].

A lower yield of MEG of 42.5%, was achieved when glucose was used as substrate. Retro-aldol condensation is not fast enough at this range of temperatures, due to the high energy barrier, therefore undesired reactions such as glucose decomposition and hydrogenation occurred, producing smaller gaseous products and sorbitol, respectively. The ratio of Ni to W in the reaction media seems to be an important factor affecting the individual steps in such a tandem reaction as it is very likely that hydrogenation reactions have higher orders than retro-aldol. Depending on the reaction conditions and substrate, one can manipulate the ratio of hydrogenation function, e.g. Ni, to retro-aldol function, e.g. W, in order to maximize the MEG yield.

Ru loaded on Zr–W mesoporous mixed oxides were evaluated for conversion of cellulose into polyols under hydrothermal conditions, 220 °C and 65 atm H₂ pressure [149]. Using a catalyst with 4.5 wt% Ru resulted in 72.2% conversion of cellulose with a MEG yield of 31.9%. Although leaching of tungsten and Ru can occur in the hydrothermal environment and cause loss of catalyst activity, the mesoporous Zr–W oxide was found to be largely stable under the hydrothermal conditions.

From an economic point of view, recoverability of catalysts from unconverted cellulose pulp will significantly reduce the consumption of energy and rare metals. Therefore, Lv et al. [172] synthesized Fe₃O₄@SiO₂/Ru–WO_x core–shell magnetically recoverable catalysts for conversion of cellulose into 1,2-PDO. These catalysts can be easily separated by applying an external magnetic field. Their results showed that Fe₃O₄@SiO₂/10%Ru–20%WO_x was more favorable than other Ru and WO_x loadings for 1,2-PDO production, with a 1,2-PDO yield of 31.4% and a

cellulose conversion of 96.8%. The presence of WO_x on Fe₃O₄@SiO₂ nanospheres led to formation of abundant Lewis acid sites that effectively catalyze glucose isomerization to fructose before glucose undergoes the retro-aldol condensation reaction.

A high-loaded (7.5 wt%) Ni single-atom catalyst, Ni–N–C, was developed for hydrothermal conversion of cellulose to MEG by Liu et al. [173]. In addition to high hydrogenation activity, this catalyst showed high durability under harsh hydrothermal conditions (245 °C, 60 atm H₂ pressure, and acidic medium). WO₃ was used to catalyze C–C cleavage of cellulose-derived sugars via the retro-aldol pathway, while Ni–N–C promoted the hydrogenation of cellulose-bearing unsaturated groups. Cellulose was converted into MEG with a yield of 36.8%. The characterizations of the used catalysts showed that single atoms of Ni were still highly dispersed and no aggregation was observed even after several experimental runs.

Xin et al. [174] synthesized and used encapsulated Co@C combined with WO₃ for MEG production from cellulose. The highest MEG yield of 67.3%, was achieved using 30 mg Co@C and 70 mg WO₃ in 20 mL aqueous medium at 245 °C under 30 atm of H₂ pressure. WO₃ mainly promoted both the cellulose hydrolysis, by acidification of water, and the retro-aldol condensation of glucose to GA, where Co@C catalysts was responsible for the hydrogenation of GA to MEG. The catalyst structure with encapsulated Co prevented the metal from poisoning and leaching under hydrothermal acid conditions.

Pang et al. [175] prepared and used 5 wt% Ru/C together with WO₃ to promote catalytic conversion of cellulose to MEG. After 2 h of reaction under hydrothermal conditions (245 °C, 50 atm H₂ pressure), cellulose was completely converted with a MEG yield of 58.4%. They also showed that 3–6 h ball milling pretreatment of lignocellulosic biomass, Miscanthus, at 450 rpm, increased the MEG yield from 22% up to about 52% relative to the whole biomass, which is comparable to the result of pure cellulose conversion.

As summarized above, cellulose can be converted into platform molecules with high selectivity through hydrothermal processes using proper catalysts. However, the process is challenged by using a low concentration of substrate in water (typically <5 wt%), harsh conditions (relatively high temperature and high H₂ pressure), leaching and coking of the catalyst.

3.2.1.2. Role of catalyst support materials. To meet industrial requirements, the active sites for catalyzing the desired reactions need to be stabilized with a suitable support material. However, the support materials may interact with the reactions directly or indirectly. Different metal oxides such as Al₂O₃, TiO₂, Nb₂O₅, ZrO₂, SiO₂, SBA-15, MCM-41, zeolites, and carbonaceous materials such as activated carbon (AC), carbon nanofibers (CNFs), and graphene have been used as support of tungsten oxide/tungsten compounds and their performance have been assessed for conversion of cellulose/glucose into glycols. The role of the support material in various supported tungsten containing catalysts for cellulose conversion have been summarized in Table 2.

Zheng et al. [155] used transition metal–tungsten bimetallic catalysts [W–M; where M is Ni, Pd, Pt, Ir, Ru, or Rh] supported on various supports for conversion of cellulose to MEG under H₂ atmosphere and hydrothermal conditions. They revealed that cooperation between C–C cracking reactions over W sites and the hydrogenation of unsaturated intermediates over the transition metals resulted in a particularly high selectivity towards MEG, up to 75% (Table 2, Entry 2). They observed a significant synergy between tungsten and metals of groups 8–10 of the periodic table. The results revealed that a W/AC catalyst was very effective for the depolymerization of cellulose, probably due to acidic environment created by acidic sites, while the monometallic M (Ni, Pd, Pt, Ir, Ru, or Rh) catalysts supported on AC were efficient for hydrogenation and even moderately selective for polyol production. Therefore, the bimetallic catalysts comprising of tungsten and another transition metal were designed to convert cellulose into MEG. It is supposed that

Table 2

Supported tungsten based catalysts used for catalytic, hydrothermal conversion of cellulose to glycols in hydrogen atmosphere.

Entry	Cellulose concentration in water (wt%) ^a	Catalyst	Reaction parameters			Conversion (%)	Yield (%)		Ref.
			T (°C)	Hydrogen pressure (atm)	Time (h)		MEG	1,2 PDO	
1	0.75	WO _x /ZrO ₂ (30 ^b ,600 ^c)+Ru/AC WO _x /ZrO ₂ (30 ^b ,750 ^c)+Ru/AC WO _x /ZrO ₂ (30 ^b ,850 ^c)+Ru/AC WO _x /ZrO ₂ (30 ^b ,900 ^c)+Ru/AC	215	52	1.5	85 90 90 88	30.6 47.2 58.8 54.0	10.5 5.1 4.5 3.6	[154]
2 ^d	1	WO ₃ +Ru/AC W/AC Ni/AC Pd/AC Pt/AC Ru/AC Ir/AC Pd-W/AC Pt-W/AC Ru-W/AC Ir-W/AC Ni-W/SiC Ni-W/TiO ₂ Ni5-W25/SBA-15	245	60	0.5	86 100 71.9 67.2 63.5 74.1 63.8 100 97.0 100 100 92.0 100 100	47.5 2.2 9.2 7.6 11.6 2.2 9.8 59.6 56.9 61.7 50.6 45.3 36.8 75.4	3.2 0.0 4.3 0.0 2.9 0.0 7.2 3.8 3.3 3.2 2.5 1.2 1.5 4.1	[155]
3	1	30 wt% W ₂ C/AC-800 60 wt% W ₂ C/AC-800 1 wt% Ni-30 wt%W ₂ C/AC-700 1 wt% Ni-30 wt%W ₂ C/AC-800 2 wt% Ni-30 wt%W ₂ C/AC-700 3 wt% Ni-30 wt%W ₂ C/AC-700	245	60	0.5	98 99 98 90 100 95	27.4 29.0 52.2 36.1 61.0 49.8	5.5 6.0 7.7 4.3 7.6 4.3	[156]
4	1	WC _x /MC WC _x /AC 2 wt% Ni-WC _x /MC 2 wt% Ni-WC _x /AC	245	60	0.5	100 100 100 100	72.9 45.7 74.4 61.7	5.1 3.6 4.5 3.4	[157]
5	2.5	3 wt% Ni-15 wt%WO ₃ /SBA-15	230	60	6	100	70.7	5.9	[160]
6	1	5 wt% Ru/graphene 30 wt% WO ₃ /graphene 5 wt% Ru-30 wt% W ₁₈ O ₄₉ /graphene	245	60	1	73.5 84.1 100	2.5 6.0 62.5	0.6 0.1 5.1	[161]
7	1	15 wt%Ni-20 wt%W/SiO ₂ 15 wt%Ni-20 wt%W/SiO ₂ -OH 15 wt%Ni-20 wt%W/γ-Al ₂ O ₃ 15 wt%Ni-20 wt%W/γ-Al ₂ O ₃ -OH 15 wt%Ni-20 wt%W/SBA-15 15 wt%Ni-20 wt%W/SBA-15-OH 15 wt%Ni-20 wt%W/ZSM-5 15 wt%Ni-20 wt%W/HZSM-5	240	50	2	90 100 76 100 85 100 71 93	32.6 63.1 21.5 51.3 28.7 59.6 17.9 42.2	3.6 2.3 1.6 1.2 3.4 2.5 2.3 1.6	[163]
8 ^e	1	Ni-W/β-zeolite+ ZnO Ni-W/β-zeolite+ MgO Ni-W/β-zeolite+ Al ₂ O ₃	245	60	0.5	100 100 100	34.3 39.8 43.3	35.8 23.2 10.7	[164]
9	1	Ni-W/SiO ₂ @C ₆ N ₄	240	50	2	100	48.3	4.2	[165]
10	1	5 wt%Al-8 wt%Ni-25 wt%W/ NaZSM-5 5 wt%Al-8%Ni-25 wt%W/ NaZSM-5 5 wt%Al-8%Ni-25 wt%W/ NaZSM-5	220	70	12 1.5 6	100 85.1 100	89 59.8 63.2	0.8 9.2 7.3	[166]
11 ^f	1	5Ni-15 W/MgAl ₂ O ₄ 5Ni-15 W-15 Cu/MgAl ₂ O ₄	245	30	2	97.7 100	33.9 52.8	6.9 8.0	[167]
12 ^{f,g}	2.5	0Al-15 W-3Ni 3Ni-15 W-3Al	230	40	1.5	87 100	56.6 76	8.4 8.3	[168]
13 ^h	1.25	TiO ₂ Ni-W/TiO ₂ Ni-W/AC MIL-125 (Ti) Ni/MIL-125 (Ti) W/MIL-125 (Ti) Ni-W/MIL-125 (Ti)	245	40	2	71.1 100 100 78.4 92.3 98.3 100	1.3 34.5 42.8 3.5 27.1 3.8 68.7	2.1 8.3 4.3 4.4 5.7 3.2 6.5	[169]
14	1.5	Pd@W/Al-MSiO ₂	240	40	1 2	94.3 95.9	53.3 55.8	5.0 5.3	[170]

^a All experiments done in batch mode; ^b tungsten wt%; ^c calcination temperature; ^d The metal loadings of monometallic catalysts were 5 wt% for the noble metal catalysts, 30 wt% for the W/AC catalyst, and 20 wt% for the Ni/AC catalyst. For bimetallic catalysts, 25 wt% of tungsten and 5 wt% of the second metal were employed in the preparation. ^e For these catalysts, the nickel and tungsten loadings were 7 wt% and 20 wt%, respectively. ^f The numbers in catalyst denotation show the metal loading in wt%. ^g TUD-1, a siliceous mesoporous material, was used as support for the catalysts. ^h The nominal weight loadings of W and Ni in all samples were 20 wt%.

retro-aldol condensation of glucose occurs over the tungsten sites and hydrogenation reactions take place on the Ni or noble-metal active sites, due to their high activity for hydrogenation reactions. A too large number of hydrogenating sites promoted the hydrogenation reactions and made them dominant over the retro-aldol reactions, leading to increased yields of hexitols and erythritol. The hexitols (mannitol and sorbitol) were found to be stable and did not form MEG when they were used as feedstock. On the contrary, very few hydrogenating sites on the catalysts resulted in small amounts of diol formation, similarly to the W/AC catalyst. Thus, there is an optimal region for the Ni/W ratio, in which the W active sites and Ni sites cooperate properly to obtain a high MEG yield. Ji et al. [156] converted cellulose to MEG over an active-carbon-supported tungsten carbide catalyst (W_2C/AC) with 27% yield to MEG. The W_2C/AC used in this work showed higher MEG yield than that of W/AC reported by Zheng et al. [155]. This is due to the fact that, transition metal carbides, i.e. W_2C have good hydrogenation properties, similar to the noble metals [176,177]. However, they showed that upon addition of an optimized amount of Ni to the W_2C catalyst (prepared by the carbothermal H_2 reduction method at 700 °C) the yield of MEG was increased up to 61% by a synergistic effect between nickel and W_2C on reactions involved in cellulose degradation. Zhang et al. [157] synthesized WC_x and $NiWC_x$ supported on mesoporous carbon (MC) to convert cellulose under hydrothermal conditions and H_2 atmosphere. Using a 2% $NiWC_x/MC$ catalyst resulted in 74.4% MEG yield, which was higher than when activated carbon was used as support by Ji et al. [156]. Compared with microporous carbon, mesoporous carbon showed advantages such as good accessibility of the pores which benefit molecular diffusion. However, the stability of the $Ni-W_2C$ catalyst presents a grand challenge for commercialization of this process since W_2C is subject to oxidation under hydrothermal reaction conditions [157,178].

Wang et al. [158] revealed that in addition to acidic sites, there is also basic sites on the WO_x/C catalyst, which enhance the isomerization of glucose to fructose in the temperature range of 180–260 °C. WO_3 was shown to be a base-free catalyst. However, their results showed that both WO_x/C and WO_3 could enhance the retro-aldol condensation of sugars, while WO_x/C in addition catalyzes the isomerization of glucose to fructose that lead to lower MEG yield. Furthermore, they demonstrated that W^{6+} was the dominant species in WO_3 with no basic sites. Introduction of Ni in the tungsten oxide structure led to formation of W^{5+} species and subsequently more basic sites and lower acidity at the $Ni-WO_x$ interface. This could enhance the isomerization and retro-aldol condensation of glucose and fructose under hydrothermal conditions in H_2 atmosphere.

Ru/graphene, WO_3 /graphene, and $Ru-W_{18}O_{49}$ /graphene nanocomposites were synthesized by solvothermolysis and used to convert 1 wt% cellulose in water into MEG at hydrothermal conditions, i.e. 245 °C and 60 atm H_2 pressure [161]. After 60 min of batch reaction, the $Ru-W_{18}O_{49}$ /graphene nanocomposite catalyst showed nearly complete conversion of cellulose with 62.5% yield of MEG. The existence of numerous $W_{18}O_{49}$ nanowires next to Ru nanoparticles on the graphene surface provided abundant active sites for selective conversion of cellulose into MEG through retro-aldol condensation and hydrogenation. However, the yield of MEG was gradually decreased after several runs due to the slow dissolution of tungsten species [161]. Ribeiro et al. investigated the effect of Ru/CNT and W/CNT mixture on one-pot conversion of woody biomass into MEG under hydrothermal conditions [179]. Under 50 atm of H_2 pressure and 205 °C, a yield of 41% of MEG relative to whole biomass was achieved after 5 h reaction. However, the presence of lignin and inorganic impurities such as divalent cations acted as poisons to the catalysts [180,181].

Xiao et al. [163] demonstrated that the existence of hydroxyl groups on the SiO_2 surface could promote the formation of Ni-W compounds (e.g. NiW , Ni_4W) in Ni-W/ SiO_2 catalysts. Formed NiW and Ni_4W were found to be very effective in retro-aldol condensation reaction and a catalyst with the composition 15 wt% Ni-20 wt% W/ SiO_2 -OH showed

the highest yield of MEG from cellulose, i.e. 63.1%, at 240 °C under 50 atm of H_2 pressure. Similar results were observed for Al_2O_3 , SBA-15, and ZSM-5 supports (Table 2, Entry 7). Zero valent Ni was also generated in higher amounts in the presence of hydroxyl groups on SiO_2 , promoting the hydrogenation of unsaturated intermediates. Moreover, embedded Ni and W in alloys were resistant against leaching in pressurized water.

A Ni-W/H-Beta zeolite in combination with ZnO was used in a batch reactor in order to convert 1 wt% cellulose in water into glycols, including MEG and 1,2-PDO [164]. 1,2-PDO forms via hydrogenation of both pyruvaldehyde and hydroxyacetone. Hydrolysis of cellulose to glucose was catalyzed by the zeolite support providing acidic conditions, while W and Ni catalyzed retro-aldol and hydrogenation reactions, respectively. However, it seems hydrolysis of cellulose is limited to the exterior part of zeolite due to the fact that transfer of microcrystalline cellulose into zeolite pores is hindered by the large size of the cellulose molecule. As discussed previously, retro-aldol reaction of glucose and subsequent hydrogenation results in MEG production. On the other hand, production of 1,2-PDO could be increased via isomerization of glucose to fructose prior to retro-aldol and hydrogenation reactions. Ni-W/H-Beta zeolite catalyst was modified with ZnO to promote isomerization of glucose to fructose, which afforded higher yields of 1,2-PDO. After 30 min reaction at 245 °C under 60 atm H_2 pressure, the yield of MEG and 1,2-PDO reached 34.3% and 35.8%, respectively. Other supports such as SiC , H-ZSM-5, TiO_2 , and Al_2O_3 were also used. However, the glucose conversion and glycols yields were lower than when using H-Beta zeolite as support. This crucial role of the H-Beta zeolite could be due to its higher acidity relative to the oxides and larger pore size relative to H-ZSM-5 enabling cellulose hydrolysis.

To protect the catalyst from hydrothermal degradation and also minimize metal leaching, Xiao et al. designed a Ni-W/ SiO_2 catalyst decorated by C_xN_y species using C- and N-sources [165]. This catalyst was used for conversion of cellulose into C_2 - C_3 oxygenates. After 2 h batch reactions, MEG and hydroxyacetone were produced with the yield of 48.25% and 20.92%, respectively, at 240 °C under 50 atm of H_2 pressure. The C_xN_y layer and formed Ni-N structures cause enhancement of resistance against sintering and acid leaching of the catalyst. Indeed, the Ni-N structure with both Lewis acid and basic sites slightly promoted the isomerization of glucose to fructose, which was subsequently converted to hydroxyacetone or pyruvaldehyde through retro-aldol condensation and hydrogenation catalyzed by W and Ni, respectively. However, hydrogenation of hydroxyacetone and pyruvaldehyde could lead to 1,2-PDO formation.

Sreekantan et al. synthesized trimetallic Al-W-Ni catalysts supported on Na-ZSM-5 and used it in a batch reactor for one-pot conversion of cellulose into MEG [166]. The maximum yield of MEG, 89%, was obtained using 5 wt% Al-8 wt% Ni-25 wt% W/Na-ZSM-5 catalyst at moderate temperature, 220 °C, and high pressure of H_2 , 70 atm, after 12 h reaction. This is the highest yield of MEG reported in the literature to the best of our knowledge. Hydrolysis of cellulose to sugar, cleavage of C-C bond for GA production, and hydrogenation of GA into MEG was reported to be facilitated in presence of Al^{3+} , $W^{5+/6+}$, and Ni, respectively.

Yu et al. investigated the synergistic effect of Ni-W-Cu on magnesium aluminum spinel ($MgAl_2O_4$) for one-pot conversion of cellulose into MEG [167]. Cellulose was converted into MEG with a yield of 52.8% after 2 h batch reaction at 245 °C under 30 atm of H_2 . The synergistic effect of Ni, W, and Cu was shown to be beneficial in cellulose conversion to MEG. Cu is efficient for hydrogenation, but to a lower extent compared to Ni, especially for hydrogenation of C-C cleaved intermediates. The presence of Cu also facilitated the reduction of W^{6+} to W^{5+} and promoted the Ni reducibility. It has been confirmed that W^{5+} shows superior effect on retro-aldol condensation compared to W^{6+} [154,158]. The interaction of Cu with W and Ni also increased the number of active W^{5+} sites and oxygen vacancies resulted in a higher degree of cleavage of C-C/C-O bonds. $MgAl_2O_4$ played an important

role as a support due to its high hydrothermal stability, hydrophobicity, mechanical strength, low surface acidity, and large number of vacant oxygen sites. The oxygen vacancies on the MgAl_2O_4 surface promoted adsorption of oxygen-containing molecules, e.g. glucose, followed by selective transformation into MEG on active metal sites in the vicinity of the adsorption sites. However, the yield of MEG decreased after several runs due to W leaching to the liquid medium.

Isolated Al^{3+} , WO_3 nanoparticles, and metallic Ni nanoparticles were incorporated into the mesoporous siliceous material, TUD-1 [168]. Cellulose hydrolysis to glucose was confirmed to occur in the presence of Al^{3+} acidic sites, with the assistance of tungsten species and H^+ formed from water at elevated temperature, above 200 °C. Oxygen vacancies in the partially reduced tungsten, WO_{3-x} , adsorbed the oxygen of glucose and catalyzed retro-aldol condensation to produce GA. GA was then hydrogenated to MEG over the nanoparticles of metallic Ni supported on TUD-1. Unlike other supports such as SBA-15, which lost about 50% of the total surface area after incorporating Mo, Ni, and Al active sites [182], the TUD-1 support maintained its high surface area of $\sim 700 \text{ m}^2/\text{g}$ after metal incorporation. Furthermore, substrates could easily reach the active sites inside the open, three-dimensional pore system of mesoporous TUD-1, react to form the products which easily desorb and diffuse out of the pore system. After 90 min reaction at 230 °C under 40 atm of H_2 pressure, the tuned catalyst containing optimized amounts of the three metals, 3 wt%Al-15 wt%W-3 wt%Ni, exhibited the highest acidity and 100% cellulose conversion with 76% MEG yield. However, as an important challenge, 16 wt% of tungsten and 7 wt% of Ni were lost from the catalyst after first run. The leached amount of aluminium into reaction media was negligible.

In order to increase the catalysts' stability during hydrothermal conversion of cellulose into MEG and maintain high conversion and selectivity, Li et al. used MIL-125 (Ti) metal-organic frameworks (MOFs) as a template for preparation of Ni-W/Ti catalysts [169]. After 2 h hydrothermal reaction (245 °C and 40 atm H_2), cellulose was completely converted with a MEG yield of 68.7%. This structure showed excellent stability and recyclability with negligible W leaching to the reaction media. The stability of this structure could be attributed to the formation of Ti–O–W bonds in which the tungsten component was connected to the catalyst support TiO_2 , resulting in minimized tungsten loss during the reaction.

Other structures, such as core-shell catalysts, have been tested for glycols production. Xin et al. synthesized a catalyst with core-shell structure composed of uniform particles of Pd as core and mesoporous SiO_2 as shell [170]. The shell was modified with one metal oxide among Mn, Mo, Co, Zn, Zr, Sn, Al, and W or with one of the bimetallic oxides W/Mn, W/Co, W/Mo, W/Zr, W/Zn, W/Sn, and W/Al. The effect of the different metal oxides on batch mode conversion of cellulose to MEG was investigated after 2 h at 240 °C and under 40 atm H_2 pressure. The highest cellulose conversion and selectivity to MEG was found to be 95.9% and 58.2%, respectively, using the Pd@W/Al- SiO_2 catalyst with W/Al molar ratio of 3.6. Among other metal oxide combinations, Pd@W/Sn- SiO_2 and Pd@W/Zr- SiO_2 compounds also showed high activity towards MEG production. This confirmed beneficial interactions between the two metal oxides, affecting the final product distribution. The acidity of the bimetallic W/Al was shown to be higher than the individual W and Al. The surface acidity of Pd@W/Al- SiO_2 increased gradually with increasing W/Al ratio from 1.2 to 4.8. Cellulose hydrolysis was increased due to the increasing catalyst acidity. Although retro-aldol condensation could be an acid-catalyzed reaction, too many acidic sites were not advantageous for the retro-aldol condensation of cellulose-derived monosaccharides due to side reactions. In another work, Xin et al. used Pd@ WO_x -mesoporous SiO_2 (Pd@ WO_x -MSiO₂) catalyst with different tungsten content for one-pot conversion of glucose into MEG [171]. The highest conversion of glucose, 99.3%, with 59.4% MEG selectivity, was achieved using Pd@ 1.5 wt% WO_x -MSiO₂ after 2 h of batch reaction at 200 °C under 50 atm of H_2 pressure. They also revealed that pore size and shell thickness affected the selectivity of

MEG production through affecting the mass transfer rate. Oxygen vacancies created by W^{5+} species increased glucose adsorption and subsequent C–C bond cleavage.

A general challenge for liquid phase reactions is leaching of the metals into the reaction environment in addition to low concentration of the substrates in water. Therefore, considerations should be made to protect active metal sites from hydrothermal degradation and leaching.

3.2.1.3. WO_x structure. It has been confirmed that interaction of tungsten oxide with the oxide supports such as Al_2O_3 , TiO_2 , Nb_2O_5 , and ZrO_2 can dramatically change the catalytic properties of tungsten oxide [144, 150]. The nature of tungsten oxide was demonstrated to be a function of tungsten oxide surface density on the support material, i.e., the number of tungsten atoms per nm^2 , and also the type of support material [150, 151]. E.g., the acidic properties of tungsten oxide on these supports is changeable by tuning the tungsten coverage over the support [150].

At low surface densities of tungsten (0.3–2.1 W/nm^2 or 2–20 wt% WO_x) highly dispersed monotonungstate as isolated WO_x , and oligomeric WO_x are formed on an Al_2O_3 support surface [151]. Isolated WO_x are the dominating species on the Pd- WO_x (5 wt%)/ Al_2O_3 catalyst. The poly-tungsten/monotungsten ratio increases with increasing tungsten oxide coverage. With further increase of the tungsten density ($>3.1 \text{ W}/\text{nm}^2$ or 30 wt% of WO_x), polymeric WO_x species and crystalline WO_3 were formed. On the other hand, the Pd surface area decreased with increasing tungsten density. Tungsten oxide species on the Al_2O_3 surface, i.e. isolated and oligomeric WO_x , were shown to be significantly more active Lewis acids sites, than the crystalline WO_3 particles. The Lewis acid sites catalyzed isomerization of glucose into fructose which subsequently underwent hydrogenolysis (Retro-aldol condensation followed by hydrogenation) to 1,2-PDO by Pd- WO_x / Al_2O_3 redox sites. At above monolayer coverage, the acidic activity of WO_3 / Al_2O_3 decreased with increasing surface tungsten content, but even at high tungsten coverage (above monolayer coverage) the acidic activity was still about one order of magnitude higher than that of bulk WO_3 . Moreover, this catalyst showed good stability during the 200 h reaction time with no leaching of Pd, but trace amounts of W species were found in the liquid samples. In the case of WO_3 supported on TiO_2 , Nb_2O_5 , and ZrO_2 , the crystalline form of WO_3 showed higher catalytic activity than the supported WO_x surface species [150]. In summary, in contrast to WO_3 / Al_2O_3 , which has a strong acidic monolayer of WO_x , the large WO_3 particles present on Nb_2O_5 , TiO_2 , and ZrO_2 supports showed higher acidity than the surface WO_x species. This could be related to the electronegativity of the support cation. With increasing support cation electronegativity ($\text{Al} > \text{Ti} \sim \text{Nb} > \text{Zr}$) [152], the acidity of WO_x monolayer and submonolayer increase as the lower electron density of the bridging W–O–support bond results in lower basic and higher acidic character. The acidic activity of WO_3 supported on TiO_2 , Nb_2O_5 , and ZrO_2 increases with increasing tungsten content and eventually gets close to that of bulk WO_3 because it forms supported bulk WO_3 particles.

Moreover, Komanoya et al. [153] revealed that there is a high density of basic sites (0.08 sites/mmol $\sim 0.0154 \text{ sites}/\text{m}^2$) on ZrO_2 compared to TiO_2 (0.006 sites/mmol $\sim 0.0006 \text{ sites}/\text{m}^2$) and Nb_2O_5 (no basicity). The density of Lewis acid sites on ZrO_2 is 0.04 sites/mmol, $\sim 0.0077 \text{ sites}/\text{m}^2$, which is substantially lower than those of Nb_2O_5 and TiO_2 with 0.15 acid sites/mmol ($\sim 0.0051 \text{ sites}/\text{m}^2$) and 0.32 acid sites/mmol ($\sim 0.0334 \text{ sites}/\text{m}^2$), respectively. One should consider high enough surface area, balanced acidity/basicity and balanced activity of the multi-functional catalyst depending on the desired product.

Chai et al. [154] investigated a WO_3 / ZrO_2 catalyst with different tungsten content in range of 20–50 wt%, particularly the effect of tungsten surface density, on hydrogenolysis of cellulose to MEG. The surface tungsten density (W/nm^2) was altered by either changing the calcination temperature or the tungsten loading. They demonstrated that the tungsten surface density increased by increasing calcination temperature, due to the decrease of the BET surface area as a result of

ZrO₂ sintering. Increasing tungsten surface density beyond monolayer coverage resulted in agglomeration of WO₃, which could more easily be reduced to W⁺⁵—OH species by H₂ compared to a monolayer of WO_x on ZrO₂, which was stabilized by interaction with the ZrO₂ support. They showed that W⁺⁵—OH species constitute the active catalytic site for cleaving the C₂–C₃ bond of the glucose molecule to form GA. The W⁵⁺ active sites have Lewis base character and catalyze the retro-aldol condensation [183]. Therefore, a higher surface density of tungsten resulted in more GA production. GA was then hydrogenated over a Ru/C catalyst to produce MEG in the same reaction pot under H₂ atmosphere.

3.2.1.4. Glucose-based processes. Glucose was also utilized as feedstock for diol production via the hydrothermal route in much research. Most of the research in this area developed based on utilizing composite catalysts comprised of active sites for retro-aldol condensation and hydrogenation. The Changchun Meihe Science and Technology Development Company patented a process for preparing diols from saccharide molecules, Fig. 10 [184]. A water-insoluble acid resistant alloy, e.g. Ni₁₀Sm₅Sn₃Al₉W₇₀Mo₅, was used as the main catalyst and a soluble tungstate or insoluble tungsten compound was used as co-catalyst to catalyze retro-aldol condensation. They operated the reactor at H₂ pressure of 50–120 bar and temperature of 150–260 °C and could reach 70% MEG yield in the process.

In a similar process, the Avantium Company successfully developed a one-step process, RAY, for conversion of carbohydrates into MEG [43]. A binary tungsten/hydrogenation catalyst, e.g. tungstic acid and Ru supported on a carrier, was designed to minimize tungsten losses and used inside a continuous stirred tank reactor with glucose aqueous solution and hydrogen as reactants.

In addition to patents, academic research was also conducted in this field. Liu et al. [151] prepared bimetallic Pd–WO_x/Al₂O₃ catalysts with ~1 wt% of Pd and different loadings of tungsten and compared their performance with WO₃, Pd/WO₃, Pd/Al₂O₃, and WO_x/Al₂O₃ in a

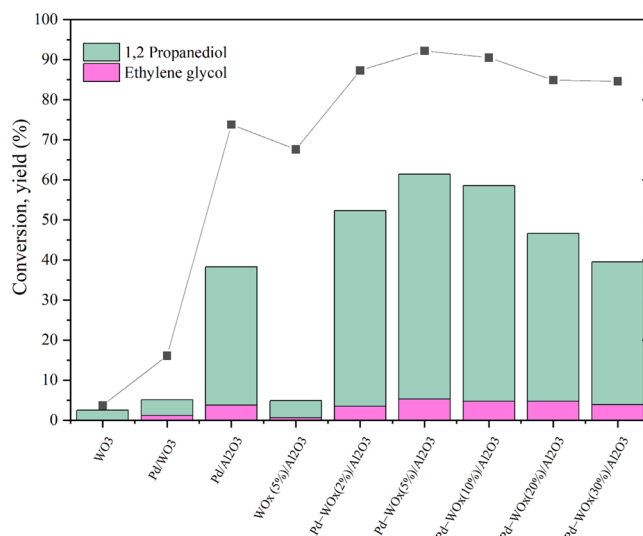


Fig. 11. Total glucose conversion and glycol yields in a fixed-bed flow reactor in the presence of different catalysts (180 °C, 40 atm of H₂ pressure, 5 wt% glucose solution; Pd loading ~1 wt%) [151].

fixed-bed flow reactor for hydrothermal conversion of a dilute aqueous glucose solution, 5 wt%. (Fig. 11 and Table 3). Among the catalysts tested, Pd(1 wt%)-WO_x(5 wt%)/Al₂O₃ showed the highest 1,2-PDO yield, i.e. 56.1%, due to the balanced concentration of Lewis acid sites and Pd metal sites.

Other catalysts used for glucose conversion at hydrothermal conditions are listed in Table 3 and discussed in the following.

Ooms et al. [71] investigated a 2 wt% Ni-30 wt% W₂C/AC catalyst in batch and fed-batch reactors to convert a glucose solution with

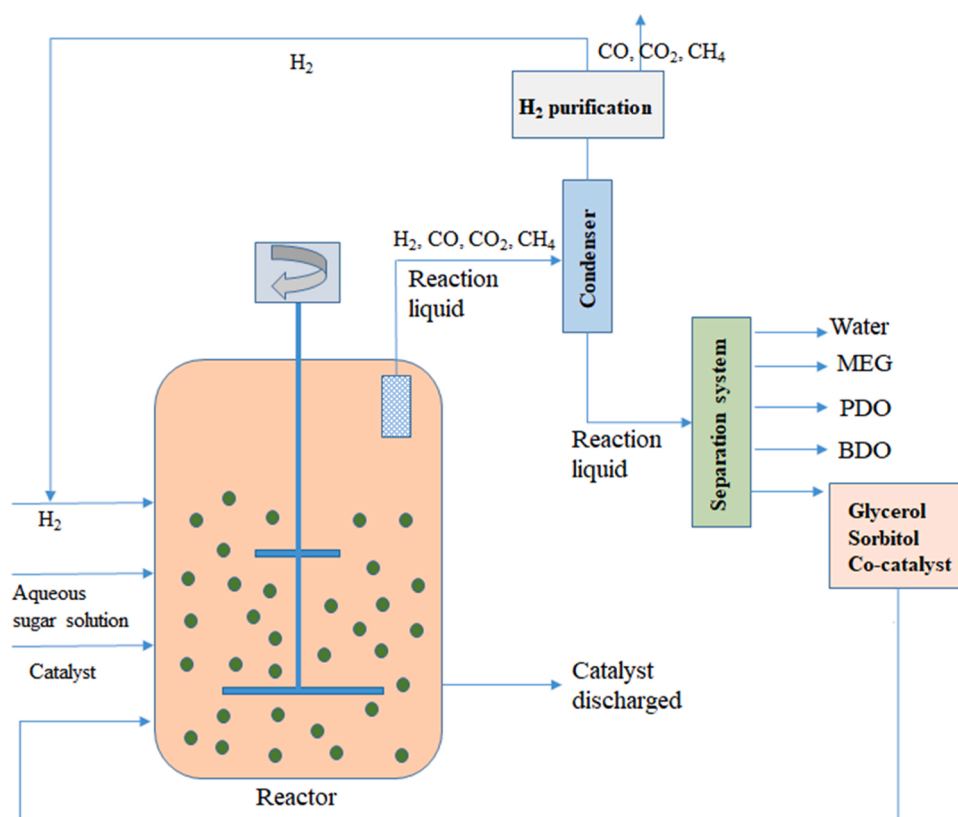


Fig. 10. One-step hydrothermal process for diol production from monosaccharide molecules [184].

Table 3

List of supported tungsten based catalysts used for catalytic, aqueous phase conversion of glucose to glycols in hydrogen atmosphere.

Entry	Glucose concentration in water (wt%) ^a	Catalyst	Reaction parameters			Conversion (%)	Yield (%)		Ref.
			T (°C)	P (atm)	Time (h)		MEG	1,2 PDO	
1	5 ^b	Pd-WO _x (2 wt%)/Al ₂ O ₃	180	40	-	87.3	3.5	48.8	[151]
		Pd-WO _x (5 wt%)/Al ₂ O ₃				92.2	5.3	56.1	
		Pd-WO _x (10 wt%)/Al ₂ O ₃				90.5	4.7	53.8	
		Pd-WO _x (20 wt%)/Al ₂ O ₃				84.9	4.7	41.9	
		Pd-WO _x (30 wt%)/Al ₂ O ₃				84.6	3.9	35.6	
2	20	2 wt%Ni-30 wt%W ₂ C/AC	245 ^c	60	3	100	47.0	4.0	[71]
			260 ^c			100	66.0	-	
			245			100	8.0	5.0	
			240			100	3.2	12.3	
3	1	Ni/C	240	40	1	100	3.2	12.3	[158]
		W-Ni/C; $\frac{W}{Ni}$ (wt. ratio) = 9.4				98.9	6.6	0.5	
4	1.25	3 wt% Ni-15 wt%WO ₃ /SBA-15	175	60	1.33	100	32.3	2.1	[159]
		5 wt% Ni-15 wt%WO ₃ /SBA-15				100	41.5	3.6	
		10% Ni-15%WO ₃ /SBA-15				100	29.8	2.4	
5	5 ^b	Ru (1 wt%)-W(10 wt%)/SiO ₂	205	40	-	100	33.8	29.2	[162]
		Ru(1 wt%)-W(10 wt%)/AC				99.3	28.7	33.0	
		Ru(1 wt%)-W(10 wt%)/CNFs				99.9	21.1	18.4	
		Ru(1 wt%)/WO ₃				87.5	48.9	11.1	
6	5 ^b	Ru (1 wt%)-W(10 wt%)/SiO ₂	190	40	-	98.2	34.6	26.6	[185]
7	1.5	Pd@ 1.5 wt%WO _x -MSiO ₂	200	50	2	99.3	59.0	14.5	[171]

^a Typically done in batch mode unless otherwise noted; ^b Fixed bed flow reactor; ^c Fed-batch reactor.

concentration of 333 g/L into MEG under H₂ pressure, see Table 3. In the fed-batch reactor a glucose solution was added to the reaction chamber during 3 h under hydrothermal conditions. The MEG yield in the fed-batch reactor (47%) was significantly higher than that of the batch reactor (8%), probably due to the higher char formation in the batch system. This was not observed when cellulose was used as substrate, as also observed by Ji et al. [156], because of the slow release of sugar during cellulose hydrolysis. Therefore, to minimize char formation one should decrease reaction time as much as possible through optimized concentration of catalyst or keep the glucose concentration low enough in order not to be in reaction-limited regime, because otherwise unreacted substrate could go in other pathways, i.e. char formation.

Cao et al. [159] used glucose to produce MEG over Ni-WO₃/SBA-15 catalysts at temperatures below 200 °C. The highest yield of MEG of 41.5% (see Table 3) was achieved using 5 wt% Ni-15 wt%WO₃/SBA-15 at 175 °C. It was presumed that the retro-aldol activity is attributed to the W oxide component of the catalyst and the hydrogenation activity is associated with the metallic Ni component of the catalyst [91,186]. With lower Ni content, the active sites for catalyzing GA hydrogenation was insufficient. However, too high loading of Ni resulted in glucose hydrogenation and decrease of MEG yield. Cao et al. [160] also showed that the catalyst reduction temperature affected the MEG yields. At higher reduction temperatures, up to 500 °C, more WO_{3-x} species (catalyzing retro-aldol condensation) could be formed leading to more MEG production. Exceeding 500 °C for catalyst reduction caused sintering of Ni species and decreased the MEG yield.

A highly dispersed Ru-WO_x catalyst supported on SiO₂ was used to convert a 5 wt% glucose aqueous solution into lower diols including MEG, and 1,2-PDO (see entry 6, Table 3) [185]. The experiments were conducted using a fixed-bed flow reactor at 190 °C and 40 atm H₂ pressure. Their results confirmed that highly dispersed (< 2 nm) WO_x clusters/particles, exposing more surface sites, promote retro-aldol reaction. An overall glucose conversion of 98.2% was obtained with 91.7% yield of total diols (MEG, 1,2-PDO, 1,2-BDO) formed through C-C bond cleavage and subsequent hydrogenation. However, the individual yields towards each diol did not exceed 35%.

In another work, Liu et al. [162] assessed Ru/WO₃ and bifunctional Ru-W catalyst supported on SiO₂, AC, and CNFs in a continuous, fixed-bed reactor to convert glucose into lower diol molecules (see entry 5, Table 3). They stated that WO_x crystallites play an important role in C-C bond cleavage in the glucose molecule. They concluded that W⁵⁺ species formed after reduction of the Ru/WO₃ catalysts and acted as

active catalytic sites for C-C bond cleavage. This was also suggested by Hamdy et al. [168], who confirmed that partially reduced W³⁺, having oxygen vacancies, can adsorb the oxygen of glucose, which facilitate rapid C-C bond cleavage and formation of intermediates such as GA. The GA can further be hydrogenated to MEG over metal sites such as Pt, Pd, and Ni. The specific surface area of the Ru/WO₃ catalyst was only 4.5 m²/g, which caused low dispersion of Ru species on the WO₃ surface. Nevertheless, numerous W⁵⁺ species as basic sites are easily generated due to the hydrogen spillover from adjacent Ru. On the other hand, highly dispersed Ru on high surface area SiO₂ support results in more sites to activate hydrogen, and the activated hydrogen generated more surface W⁴⁺ species. Since acidity is a major parameter affecting various reactions, e.g. isomerization and dehydration, it seems that the Ru(1 wt%)/WO₃ catalyst with lower acidity has suppressed these reactions. Therefore, a higher yield of MEG when using the Ru (1 wt %)/WO₃ catalyst, in comparison with other Ru-W catalysts, could be related to the fact that more retro-aldol reaction occurs in competition with isomerization and dehydration reactions. However, the stability of Ru-W/SiO₂ and its resistance against leaching was better than that of Ru/WO₃ over time. Therefore, the acid-base balance on the catalyst must be tuned to increase the selectivity to the desired MEG, while maximizing the conversion of glucose and the stability of the catalyst.

Similar to cellulose substrate, the hydrothermal conversion of glucose is challenged by low concentration of substrate in water, harsh operating conditions, leaching and coking of the catalyst.

3.2.2. Other heterogeneous, non-tungstic catalysts

Non-tungstic catalysts, having different functionalities have been examined for cellulose and glucose conversion into polyols at hydrothermal conditions (Fig. 12).

Li et al. [95] designed a Co/CeO_x catalyst with both basic and acidic sites for one-pot conversion of 1 wt% cellulose in water into MEG and 1, 2-PDO. The Coⁿ⁺-O_x-Ce³⁺ pair was formed and efficiently catalyzed retro-aldol condensation, isomerization, and hydrogenation reactions, having both acidic and mildly basic sites exerted by Co and Ce, respectively. In the presence of hot water, the Coⁿ⁺-O_x-Ce³⁺ pair provided enough acidic sites for efficient hydrolysis of cellulose. Increasing the Co loading led to an increase in the number of acidic sites due to the increase of surface metallic Co sites and/or Coⁿ⁺-O_x-Ce³⁺ sites. However, increasing the Co loading also resulted in a decrease in the number of basic sites due to Co covering the CeO_x surface. Using an optimized 10 wt% Co/CeO_x catalyst at hydrothermal conditions,

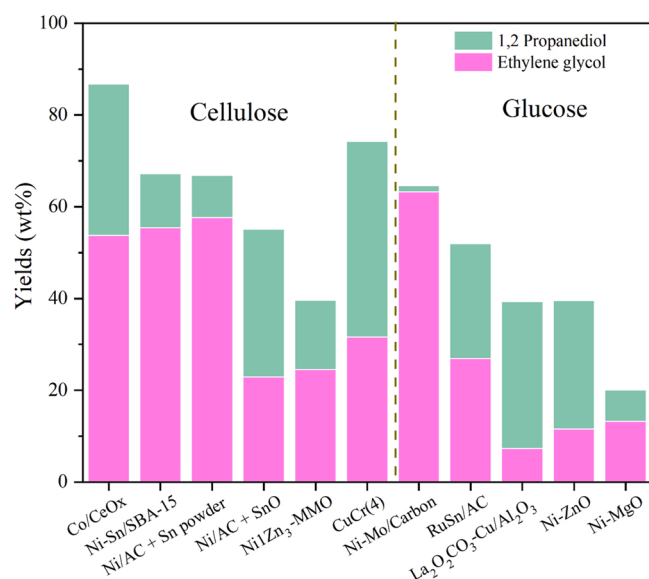


Fig. 12. Hydrothermal conversion of cellulose and glucose into glycols in presence of different catalysts not containing tungsten [65,95,187–192].

245 °C, 30 atm H₂, and 6 h reaction time, resulted in MEG and 1,2-PDO yields of 53.7% and 33.0%, respectively, see Fig. 12. The slightly basic environment restricted glucose reaction to humins. Furthermore, low accumulation of glucose due to the controlled hydrolysis rate of cellulose was also effective for suppressing unwanted reactions, i.e. glucose hydrogenation and humin formation. Exceeding the optimal Co loading of 10 wt%, created more acidic and less basic sites, resulting in lower diol yields.

A bimetallic Ni-Sn catalyst supported on SBA-15 was used for one-pot conversion of 0.9 wt% cellulose in water to C₂-C₃ polyols [187]. The catalyst with composition 10 wt% Ni-15 wt% Sn/SBA-15 achieved the highest yield of MEG of 55.4% after 2 h reaction at 245 °C under 50 atm of H₂ pressure. It was revealed that Sn species in combination with SnNi alloys catalyzed C-C/C-O bond cleavage, i.e. retro-aldol condensation, of monosaccharides derived from cellulose.

Sun et al. synthesized 20 wt% Ni catalysts supported on various materials including AC, Al₂O₃, MgO, ZnO, TiO₂, and SiO₂ [188]. According to their results, the combination of Ni/AC and metallic SnO powder exhibited a superior activity toward cellulose conversion with 57.6% yield of MEG. NiSn alloy formed from metallic Ni and Sn powder under reaction conditions, i.e. 245 °C and 50 atm H₂. On the other hand, the combination of Ni/AC and SnO powder favored the formation of 1, 2-PDO as the dominant product with a yield of 32.2%. This is due to the fact that both NiSn alloy and SnO were confirmed to be effective for the retro-aldol reaction of glucose. SnO was found to be active also for isomerization of glucose to fructose, which resulted in 1,2-PDO formation as a consequence of retro-aldol reaction and hydrogenation of fructose. Therefore, one may control the glycol product distribution using SnO or NiSn alloy as active sites. Compared to the Ni/AC, other supported catalysts, i.e. Ni/Al₂O₃, Ni/MgO, Ni/ZnO, Ni/TiO₂, and Ni/SiO₂ showed much lower selectivity towards MEG and 1,2-PDO. However, among them, Ni/ZnO and Ni/MgO showed notable promotion of MEG and 1,2-PDO formation, which could be attributed to the catalytic effect of ZnO and MgO supports on isomerization and retro-aldol reactions.

Gao et al. [191] synthesized mixed metal oxide catalysts Ni-MMO and NiZn-MMO to catalyze cellulose conversion to polyols at 240 °C under 40 atm H₂ pressure. They showed that ZnO in the NiZn-MMO catalyzes the isomerization reaction, promoting the formation of more 1,2-PDO. The strong interaction between Ni and Zn inhibits the dissolution of the Ni metal in the hydrothermal reaction medium, giving

excellent recycling performance.

Xiao et al. [192] synthesized copper chromium (CuCr) catalysts with different Cu/Cr ratio for direct conversion of highly concentrated cellulose (up to 15 wt%) into 1,2-PDO and MEG in aqueous medium. Up to 10 wt% cellulose was completely converted, with a yield of 36.3% 1, 2PDO as the main product. Their study indicated that addition of Ca (OH)₂ as co-catalyst resulted in significant increase in the MEG yield. The maximum yields of 1,2-PDO and MEG were 42.6% and 31.6% over CuCr(4), Cu/Cr = 4.9 mass ratio, catalyst with 2000 ppm Ca(OH)₂.

Pang et al. synthesized a series of RuSn/AC catalysts with 5 wt% Ru and 1–6 wt% of Sn loading for conversion of a 10 wt% aqueous glucose solution to 1,2-PDO and MEG in a semi-continuous autoclave reactor [65]. A 5 wt% Ru-3 wt%Sn/AC catalyst was found to have the optimum composition in which 77% of the Sn was in the form of a RuSn alloy and the remaining 23% was in the form of highly dispersed SnO₂. After 10 min reaction, the catalyst gave 25% and 26.9% yields of 1,2-PDO and MEG at 240 °C under 50 atm of H₂ pressure. The highly dispersed SnO₂ showed activity for glucose isomerization to fructose, while the RuSn alloy played a major role in retro-aldol condensation and hydrogenation reactions.

The base properties of lanthanum oxycarbonate modified Cu/Al₂O₃ catalysts and their performance on aqueous hydrogenolysis of glucose to 1,2-PDO was investigated by Yazdani et al. [190]. The basicity of the catalyst was shown to catalyze the isomerization of glucose to fructose and the C-C bond cleavage of fructose. A balance of base sites and hydrogenation sites was also required to promote glucose hydrogenolysis and minimize unwanted hexitols production as a result of sugar hydrogenation. After 10 min reaction at 200 °C under 34 atm of H₂ pressure and in presence of an optimized La₂O₃-CO₃-Cu/Al₂O₃ catalyst, a glucose solution (0.3 wt% in water) was completely converted with MEG and 1,2-PDO yields of 7.1% and 32% respectively. Lactic acid, glycerol, sorbitol, ethanol, 1,2-butanediol, erythritol, methanol, 2, 5-hexandiol, 2,5-hexanedione, levulinic acid, arabinol, fructose, and xylitol were among the main byproducts of the reaction, respectively.

Ni-MgO and Ni-ZnO catalysts were prepared by co-precipitation in order to investigate the role of support in glucose conversion to 1,2-PDO and MEG at hydrothermal conditions (220 °C and 60 atm of H₂ pressure) [189]. Based on the results, both MgO and ZnO supports facilitated the glucose isomerization to fructose and retro-aldol condensation of fructose at the C3-C4 position to form C₃ products. Production of 1, 2-PDO was favored over MEG in the presence of MgO and ZnO supports. The reason is that glucose is converted to fructose which is quickly converted to 1,2-PDO which pulls the glucose-fructose equilibrium towards fructose.

Kirali et al. studied effects of Ni-Mo/mesoporous carbon catalysts on the conversion of glucose (15 wt% solution) into MEG under hydrothermal conditions in a batch reactor [193]. After 6 h reaction at 200 °C under 50 atm of H₂ pressure, a catalyst with 3 wt% Ni and 15 wt% Mo on mesoporous carbon resulted in complete conversion of glucose with 63.2% MEG yield. This yield was higher than that of catalysts with Ni and W in the formulation reported in Table 3 for batch conversion of glucose. They showed that Mo was highly dispersed in the presence of Ni, leading to partial reduction of Mo to lower oxidation states (+5 and +4). Partially reduced Mo catalysts led to faster retro-aldol reaction followed by hydrogenation catalyzed by Ni.

In another study, Ni-Mo bimetallic catalysts with different loadings on an Al₂O₃ support were synthesized to test their catalytic activity towards sucrose to 1,2-PDO conversion [194]. The Ni-Mo/ γ -Al₂O₃ with 8 wt% Ni and 20 wt% loading was found to be effective in producing a high yield of 1,2-PDO (~74%) under mild reaction conditions of 180 °C, 40 bar H₂ pressure and a run time of 4.5 h in a batch reactor. They showed that the Lewis to Brønsted acid site ratio is responsible for the selectivity in conversion of sucrose to 1,2-PDO.

In addition to acid sites, it has been confirmed that basic sites are capable of catalyzing retro-aldol condensation reactions and also preventing humin formation [190,195–197]. All alkaline and alkaline-earth

metals, ammonium hydroxide, basic ammonium salts, basic organics typically containing N, and solid bases are effective for retro-aldol condensation of sugars [77,197]. However, the initial acid-catalyzed cellulose hydrolysis to sugars is limited by basic sites, resulting in a decrease of the overall performance when introducing basic sites in the catalyst. Adding a very small amount of base to promote C–C bond cleavage in glucose without affecting the cellulose hydrolysis significantly could be a solution. As an alternative, one can directly use sugars as feedstock to bypass the hydrolysis step. On the other hand, basic sites for MEG production is limited due to their activity for glucose isomerization to fructose which lead to 1,2-PDO as the main product instead of MEG [78]. Therefore, depending on feedstock type, cellulose or glucose, and the desired product, the presence, strength and number of basic sites in balance with acidic sites should be taken into account.

4. Conclusions and outlook

Efficient conversion of lignocellulosic biomass into valuable molecules is a necessity of our society to completely shift away from fossil-based to renewable resources. Despite significant progress in the development of catalytic/non-catalytic processes, selective transformation of lignocellulosic biomass is still challenging due to the complex reaction pathways involving multiple reaction steps of several substrates (hemicellulose, cellulose and lignin). High energy requirements and practical obstacles such as coke formation and catalyst deactivation are among the most important challenges for these processes. Separation of lignocellulose to its main parts cellulose, hemicellulose, and lignin, followed by subsequent transformation of each part is considered an attractive strategy to increase the efficiency of chemicals production. Conversion of cellulose, the most abundant part, and cellulose-derived sugars has been studied intensively.

Herein we reviewed several possible products that could be derived from cellulose and its building block glucose, focusing on important platform molecules, particularly glycolaldehyde (GA) and the glycols including mono ethylene glycol (MEG) and 1,2-propanediol (1,2-PDO). Production of these platform molecules through hydrothermal and (catalytic) pyrolysis has attracted great attention. Transformation of cellulose and glucose to glycols have been divided into two main paths including hydrous pyrolysis and hydrothermal liquid phase processes looking into both academic research and patents. The main reactions and possible pathways involved in the cellulose/glucose transformation were discussed under both hydrothermal and pyrolysis conditions.

Pyrolysis of cellulose and glucose at dry condition led to formation of a wide product distribution including levoglucosan, 1,6-anhydroglucofuranose, dianhydroglucopyranose, furfural, 5-HMF, furan-3-methanol, 2,5-dimethylfuran, methylglyoxal, hydroxyacetone, GA, formic acid, formaldehyde, char and permanent gases. Although the yield strongly depends on specific operating conditions such as heating rate and sample size, the selectivity of cellulose/glucose dry pyrolysis towards specific molecules is not high enough to be industrially relevant. Specifically, the GA yield did not exceed 20 wt%. Furthermore, as expected, MEG and 1,2-PDO were not among the products due to the absence of hydrogen. Therefore, biomass dry pyrolysis holds great potential only for production of biofuel in which a wide range of hydrocarbons are within the target range and not for chemicals, e.g. GA or diols production. On the other hand, the use of an aqueous solution of sugars at pyrolysis condition, hydrous pyrolysis, alter the product distribution significantly with substantially improved GA yield, up to 80 wt%. The presence of water facilitated pericyclic fragmentation reactions of carbohydrates and minimized reactions such as formation of cyclic anhydrosugars, char and permanent gases. Low residence time (< 2 s) and relatively high temperature (> 500 °C) favored the highly endothermic retro-aldol reactions with high energy barrier to occur to a higher extent than competing reactions. However, this method is only applicable for sugars that can be dissolved in water. A further advantage is that high concentrations of glucose (up to solubility limit) can be used without

adverse effects on the yield of GA. Therefore, hydrous pyrolysis of glucose could be a promising approach to produce GA, as the immediate product of glucose retro-aldol condensation, and MEG through subsequent hydrogenation. Although the type of bed material in the fluidized bed plays an important role affecting the yield of GA, most of the bed materials used in hydrous pyrolysis are catalytically inert that resulted in GA as a dominant product. An active catalyst which is capable of catalyzing retro-aldol reactions and has high mechanical strength for application in a fluidized bed reactor could help this reaction to occur more selectively and at milder conditions, which would increase its economic competitiveness for GA production. Furthermore, a catalyst having isomerization activity can change the reaction network direction towards pyruvaldehyde production through initial glucose to fructose isomerization. Fructose then undergoes retro-aldol condensation to pyruvaldehyde. Pyruvaldehyde can be hydrogenated into 1,2-PDO in a subsequent hydrogenation step. However, 1,2-PDO production through hydrous pyrolysis has not been reported in the literature. The GA yield from hydrous pyrolysis was generally higher than the glycol yields achieved using catalytic hydrothermal processes, which were tested mostly in batch mode with residence time on the order of hours. However, the optimum working temperature of hydrous pyrolysis is in the range of 500–550 °C. Therefore, developing catalytic hydrous pyrolysis and hydrolysis of sugars operating at lower temperatures could be considered as a promising route to produce small oxygenates, such as MEG and 1,2 PDO, in a more efficient way.

The advances in conversion of cellulose and cellulose-derived sugars into value-added chemicals by hydrothermal processes were also discussed in this review. Cellulose and cellulose derived glucose could be converted into various platform molecules, including both MEG and 1,2-PDO in one step, with high selectivity through hydrothermal processes using proper catalysts. This process operates at lower temperature than required by pyrolysis-based processes, 200–250 °C in the presence of high-pressure hydrogen, typically 30–70 bar. The desired reactions in a competitive reaction network are catalyzed by specific catalytic active sites. Coupling of the desired reactions occurring in series and balancing their rates using multi-functional catalysts is crucial to obtain a high product selectivity. For MEG production three main reactions, hydrolysis of cellulose to glucose, retro-aldol condensation of glucose to GA, and hydrogenation of GA to MEG are needed to be catalyzed with matched rates. While, for 1,2-PDO as a target diol, isomerization of glucose to fructose is needed prior to retro-aldol condensation. Fructose, subsequently undergoes retro-aldol condensation to produce hydroxyacetone or pyruvaldehyde. Hydrogenation of both hydroxyacetone and pyruvaldehyde could lead to 1,2-PDO. The fundamental understanding of reaction pathways as well as the involved intermediates and their interaction with the catalytically active sites is required to develop the correlations between catalyst structure and process performance and to guide the catalyst development. However, knowledge of the relative rates of parallel and consecutive reactions occurring during the conversion process needs to be increased. Furthermore, the process is challenged by using low concentrations of substrate in water (typically < 5 wt%), harsh conditions (moderate temperature of typically 240 °C and high H_2 pressure of 30–70 bar), leaching and coking of the catalyst. Differently designed catalysts were surveyed to highlight the relationships between catalyst structure and its activity towards production of target molecules. The retro-aldol reaction plays an important role in the formation of glycols from cellulose-derived sugars in pyrolysis and hydrothermal processes. This highly endothermic reaction is favored by elevated temperatures, like those in the hydrous pyrolysis process. However, too high temperatures favor humin formation in hydrothermal processes. Using efficient catalysts for the retro-aldol reaction, often Lewis basic catalysts, particularly partly reduced tungsten oxide and various other tungsten compounds, $Pd-WO_x$, $Pt-WO_x$, $Ru-WO_x$, $Ir-WO_x$, $Ni-WO_x$, $Ni-W_2C$, but also partly reduced Ce, Sn, La or Mo oxide or basic oxides such as MgO and ZnO, promotes this reaction to take place efficiently, increasing the economic competitiveness of the process.

However, at milder temperatures several reactions with low energy barrier could happen, highlighting the importance of catalyst composition and structure in directing the desired reactions. For example, too many hydrogenating sites promoted the hydrogenation reactions of the sugars and make them dominant over the retro-aldol reactions, leading to increased yields of reduced sugars such as hexitols and erythritol instead of small glycols. On the other hand, catalyst composition, metallic phases, surface structure, acid/base balance, etc. could be changed under reaction conditions affecting the overall activity. Therefore, one should note the changes of the catalysts during operation through monitoring the catalyst using in-situ characterization techniques, to understand the full aspects of the catalyst. This will help to design catalysts with high stability and achieve uniform/steady production during long-term operation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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References

- [1] G. Velvizhi, C. Goswami, N.P. Shetti, E. Ahmad, K. Kishore Pant, T. M. Aminabhavi, Valorisation of lignocellulosic biomass to value-added products: Paving the pathway towards low-carbon footprint, *Fuel* 313 (2022), 122678, <https://doi.org/10.1016/J.FUEL.2021.122678>.
- [2] J. Ma, S. Shi, X. Jia, F. Xia, H. Ma, J. Gao, J. Xu, Advances in catalytic conversion of lignocellulose to chemicals and liquid fuels, *J. Energy Chem.* 36 (2019) 74–86, <https://doi.org/10.1016/J.JEACHEM.2019.04.026>.
- [3] S. van den Bosch, S.-F. Koelwijn, T. Renders, G. van den Bossche, T. Vangeel, W. Schutyser, B.F. Sels, Catalytic strategies towards lignin-derived chemicals, *Top. Curr. Chem.* 376 (2018) 1–40.
- [4] K. Qin, W. Lin, P.A. Jensen, A.D. Jensen, High-temperature entrained flow gasification of biomass, *Fuel* 93 (2012) 589–600.
- [5] A. Eschenbacher, A. Saracian, P.A. Jensen, B.H. Shanks, C. Li, J.O. Duus, T.E. L. Smitshuysen, C.D. Damsgaard, A.B. Hansen, K.I. Kling, Deoxygenation of wheat straw fast pyrolysis vapors over Na-Al₂O₃ catalyst for production of bio-oil with low acidity, *Chem. Eng. J.* 394 (2020), 124878.
- [6] A.T. Hoang, H.C. Ong, I.M.R. Fattah, C.T. Chong, C.K. Cheng, R. Sakthivel, Y.S. Ok, Progress on the lignocellulosic biomass pyrolysis for biofuel production toward environmental sustainability, *Fuel Process. Technol.* 223 (2021), 106997.
- [7] T.M.H. Dabros, M.Z. Stummann, M. Høj, P.A. Jensen, J.-D. Grunwaldt, J. Gabrielsen, P.M. Mortensen, A.D. Jensen, Transportation fuels from biomass fast pyrolysis, catalytic hydrodeoxygenation, and catalytic fast hydropyrolysis, *Prog. Energy Combust. Sci.* 68 (2018) 268–309.
- [8] D.C. Elliott, P. Biller, A.B. Ross, A.J. Schmidt, S.B. Jones, Hydrothermal liquefaction of biomass: developments from batch to continuous process, *Bioresour. Technol.* 178 (2015) 147–156.
- [9] M.Z. Stummann, M. Høj, J. Gabrielsen, L.R. Clausen, P.A. Jensen, A.D. Jensen, A perspective on catalytic hydropyrolysis of biomass, *Renew. Sustain. Energy Rev.* 143 (2021), 110960.
- [10] M.Z. Stummann, M. Høj, B. Davidsen, A.B. Hansen, L.P. Hansen, P. Wiwel, C. B. Schandel, J. Gabrielsen, P.A. Jensen, A.D. Jensen, Effect of the catalyst in fluid bed catalytic hydropyrolysis, *Catal. Today* 355 (2020) 96–109.
- [11] F.L.P. Resende, Recent advances on fast hydropyrolysis of biomass, *Catal. Today* 269 (2016) 148–155, <https://doi.org/10.1016/J.CATTOD.2016.01.004>.
- [12] F.H. Isikgor, C.R. Becer, Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers, *Polym. Chem.* 6 (2015) 4497–4559.
- [13] C.-H. Zhou, X. Xia, C.-X. Lin, D.-S. Tong, J. Beltramini, Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels, *Chem. Soc. Rev.* 40 (2011) 5588–5617.
- [14] H. Li, A. Riisager, S. Saravanamurugan, A. Pandey, R.S. Sangwan, S. Yang, R. Luque, Carbon-increasing catalytic strategies for upgrading biomass into energy-intensive fuels and chemicals, *ACS Catal.* 8 (2018) 148–187.
- [15] L. Ye, Y. Han, X. Wang, X. Lu, X. Qi, H. Yu, Recent progress in furfural production from hemicellulose and its derivatives: Conversion mechanism, catalytic system, solvent selection, *Mol. Catal.* 515 (2021), 111899, <https://doi.org/10.1016/J.MCAT.2021.111899>.
- [16] N.W. Dulie, B. Woldeyes, H.D. Demsash, A.S. Jabasingh, An Insight into the Valorization of Hemicellulose Fraction of Biomass into Furfural: Catalytic Conversion and Product Separation, *Waste Biomass-- Valoriz.* 12 (2021) 531–552, <https://doi.org/10.1007/S12649-020-00946-1>.
- [17] C. Espro, B. Gumina, T. Szumelda, E. Paone, F. Mauriello, Catalytic Transfer Hydrogenolysis as an Effective Tool for the Reductive Upgrading of Cellulose, Hemicellulose, Lignin, and Their Derived Molecules, *Page 313. 8, Catalysts* 2018, Vol. 8 (2018) 313, <https://doi.org/10.3390/CATAL8080313>.
- [18] I. Delidovich, K. Leonhard, R. Palkovits, Cellulose and hemicellulose valorisation: an integrated challenge of catalysis and reaction engineering, *Energy Environ. Sci.* 7 (2014) 2803–2830, <https://doi.org/10.1039/C4EE01067A>.
- [19] P. Rapado, L. Faba, S. Ordóñez, Influence of delignification and reaction conditions in the aqueous phase transformation of lignocellulosic biomass to platform molecules, *Bioresour. Technol.* 321 (2021), 124500, <https://doi.org/10.1016/J.BIORTECH.2020.124500>.
- [20] Z. Huang, J. Chen, Y. Jia, H. Liu, C. Xia, H. Liu, Selective hydrogenolysis of xylitol to ethylene glycol and propylene glycol over copper catalysts, *Appl. Catal. B* 147 (2014) 377–386, <https://doi.org/10.1016/J.APCATB.2013.09.014>.
- [21] J. Park, U. Mushtaq, J.R. Sugiarto, D. Verma, J. Kim, Total chemocatalytic cascade conversion of lignocellulosic biomass into biochemicals, *Appl. Catal. B* 310 (2022), 121280, <https://doi.org/10.1016/J.APCATB.2022.121280>.
- [22] M. Yabushita, H. Kobayashi, A. Fukuoka, Catalytic transformation of cellulose into platform chemicals, *Appl. Catal. B* 145 (2014) 1–9.
- [23] Y. Wu, H. Wang, J. Peng, M. Ding, Advances in catalytic valorization of cellulose into value-added chemicals and fuels over heterogeneous catalysts, *Catal. Today* (2022), <https://doi.org/10.1016/J.CATTOD.2022.08.012>.
- [24] N. Enjamuri, S. Darbha, Adv. Catal. Convers. Lignocellul. Biomass-- Ethyl. glycol (2022) 1–71, <https://doi.org/10.1080/01614940.2022.2111070>. (<https://doi.org/10.1080/01614940.2022.2111070>).
- [25] O. v. Manaenkov, O. v. Kisilitsa, V.G. Matveeva, E.M. Sulman, M.G. Sulman, L. M. Bronstein, Cellulose Conversion Into Hexitols and Glycols in Water: Recent Advances in Catalyst Development, *Front Chem.* 7 (2019) 834, <https://doi.org/10.3389/FCHEM.2019.00834/BIBTEX>.
- [26] J. Ma, S. Shi, X. Jia, F. Xia, H. Ma, J. Gao, J. Xu, Advances in catalytic conversion of lignocellulose to chemicals and liquid fuels, *J. Energy Chem.* 36 (2019) 74–86, <https://doi.org/10.1016/J.JEACHEM.2019.04.026>.
- [27] Z. Yuan, W. Dai, S. Zhang, F. Wang, J. Jian, J. Zeng, H. Zhou, Heterogeneous strategies for selective conversion of lignocellulosic polysaccharides, *6. 29, Cellulose* 2022 (29) (2022) 3059–3077, <https://doi.org/10.1007/S10570-022-04434-8>.
- [28] P. Sudarsanam, N.K. Gupta, B. Mallesham, N. Singh, P.N. Kalbande, B.M. Reddy, B.F. Sels, Supported MoO_x and WO_x solid acids for biomass valorization: interplay of coordination chemistry, acidity, and catalysis, *ACS Catal.* 11 (2021) 13603–13648, <https://doi.org/10.1021/ACSCATAL.1C03326>.
- [29] Y. Wu, H. Wang, J. Peng, M. Ding, Advances in catalytic valorization of cellulose into value-added chemicals and fuels over heterogeneous catalysts, *Catal. Today* 408 (2023) 92–110, <https://doi.org/10.1016/J.CATTOD.2022.08.012>.
- [30] N.D. Fitzgerald, Chemistry challenges to enable a sustainable bioeconomy, *10. 1, Nat. Rev. Chem.* 2017 (1) (2017) 1–3, <https://doi.org/10.1038/s41570-017-0080>.
- [31] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Techno-economic analysis of monosaccharide production via fast pyrolysis of lignocellulose, *Bioresour. Technol.* 127 (2013) 358–365, <https://doi.org/10.1016/J.BIORTECH.2012.09.070>.
- [32] P.D.T. Y. K N, K.S. S. P, S. Y.K. R, S. Varjani, G. AdishKumar, R.B.J. Kumar, Lignocellulosic biomass-based pyrolysis: A comprehensive review, *Chemosphere* 286 (2022), 131824, <https://doi.org/10.1016/J.CHEMOSPHERE.2021.131824>.
- [33] A. Kohler, W. Seames, C. Shaffer, C. Bjerke, J. Dahl, Techno-Economic Analysis of a Process for the Aqueous Conversion of Corn Stover into Lactic and Levulinic Acid through Sn-Beta Catalysis, *Page 436. 9, Processes* 2021, Vol. 9 (2021) 436, <https://doi.org/10.3390/PR9030436>.
- [34] R.F. Beims, Y. Hu, H. Shui, C. (Charles) Xu, Hydrothermal liquefaction of biomass to fuels and value-added chemicals: Products applications and challenges to develop large-scale operations, *Biomass Bioenergy* 135 (2020), 105510, <https://doi.org/10.1016/J.BIOMBIOE.2020.105510>.
- [35] J.J. Wiesfeld, P. Persolija, F.A. Rollier, A.M. Elemans-Mehring, E.J.M. Hensen, Cellulose conversion to ethylene glycol by tungsten oxide-based catalysts, *Mol. Catal.* 473 (2019), 110400.
- [36] CelluAPP® - SEKAB, (n.d.). (<https://www.sekab.com/en/products-services/product/celluapp/>) (accessed December 14, 2021).
- [37] (12) International Application Published Under the Patent Cooperation Treaty (PCT) (19) World Intellectual Property Organization International Bureau © v (54) Title: RAPID PRETREATMENT o, 2016.
- [38] Sweetwater Energy Process | Sweetwater Energy, (n.d.). (<https://www.sweetwater.us/process/>) (accessed December 14, 2021).
- [39] Renmatix Turns Biomass into Sugars for Industrial Use – Farm Energy, (n.d.). (<https://farm-energy.extension.org/renmatix-turns-biomass-into-sugars-for-industrial-use/#Research%20Purpose>) (accessed December 14, 2021).
- [40] Process - Bio-Sep, (n.d.). (<https://bio-sep.com/process/>) (accessed December 14, 2021).
- [41] M. Iakovlev, S. Survase, L. Hill, S. Sideri, S. Rouzinou, P. Kroff, V. Pylkanen, S. Rutherford, T. Retina, Pilot scale sulfur dioxide-ethanol-water fractionation of

- recycled wood to sugars, bioethanol, lignin and lignosulfonates: Carbohydrate balance, *Bioresour. Technol.* 307 (2020), 123240, <https://doi.org/10.1016/j.biortech.2020.123240>.
- [42] R. van Putten, B. McKay, G.J.M. Gruter, J.C. van der Waal, Process for the conversion of a solid lignocellulosic material, 2021.
- [43] J.C. van der Waal, G.J.M. Gruter, Process for preparing ethylene glycol from a carbohydrate, 2018.
- [44] Avantium entering the commercialization phase for PEF - bioplastics MAGAZINE, (n.d.). (<https://www.bioplasticsmagazine.com/en/news/meldungen/07062019-Avantiumentering-the-commercialization-phase-for-PEF.php>) (accessed December 14, 2021).
- [45] W.H. Faveere, S. van Praet, B. Vermeeren, K.N.R. Dumoleijn, K. Moonen, E. Taarning, B.F. Sels, Toward Replacing Ethylene Oxide in a Sustainable World: Glycolaldehyde as a Bio-Based C2 Platform Molecule, *Angew. Chem.* 133 (2021) 12312–12331.
- [46] M. Sherbi, A. Wesner, V.K. Wisniewski, A. Bukowski, H. Velichkova, B. Fiedler, J. Albert, Superior CNT-supported bimetallic RuCu catalyst for the highly selective hydrogenolysis of glycerol to 1, 2-propanediol, *Catal. Sci. Technol.* 11 (2021) 6649–6653.
- [47] Y. Cao, J. Wang, M. Kang, Y. Zhu, Catalytic conversion of glucose and cellobiose to ethylene glycol over Ni-WO₃/SBA-15 catalysts, *RSC Adv.* 5 (2015) 90904–90912.
- [48] Y. Zhang, T. Chen, G. Zhang, G. Wang, H. Zhang, Efficient production of isosorbide from sorbitol dehydration over mesoporous carbon-based acid catalyst, *Appl. Catal. A Gen.* 575 (2019) 38–47.
- [49] A. Herbst, C. Janiak, Selective glucose conversion to 5-hydroxymethylfurfural (5-HMF) instead of levulinic acid with MIL-101Cr MOF-derivatives, *N. J. Chem.* 40 (2016) 7958–7967.
- [50] Y. Jia, H. Liu, Mechanistic insight into the selective hydrogenolysis of sorbitol to propylene glycol and ethylene glycol on supported Ru catalysts, *Catal. Sci. Technol.* 6 (2016) 7042–7052.
- [51] G.M. Lari, C. Mondelli, J. Pérez-Ramírez, Gas-phase oxidation of glycerol to dihydroxyacetone over tailored iron zeolites, *ACS Catal.* 5 (2015) 1453–1461.
- [52] E.G. Rodrigues, M.F.R. Pereira, J.J. Delgado, X. Chen, J.J.M. Órfão, Enhancement of the selectivity to dihydroxyacetone in glycerol oxidation using gold nanoparticles supported on carbon nanotubes, *Catal. Commun.* 16 (2011) 64–69.
- [53] A. Villa, N. Dimitratos, C.E. Chan-Thaw, C. Hammond, L. Prati, G.J. Hutchings, Glycerol oxidation using gold-containing catalysts, *Acc. Chem. Res.* 48 (2015) 1403–1412.
- [54] M. Sajid, X. Zhao, D. Liu, Production of 2, 5-furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural (HMF): recent progress focusing on the chemical-catalytic routes, *Green. Chem.* 20 (2018) 5427–5453.
- [55] S. Nanda, D.-V.N. Vo, P.K. Sarangi, Biorefinery of Alternative Resources: Targeting Green Fuels and Platform Chemicals, Springer Nature, 2020.
- [56] A. Cabioc, E. Guillon, F. Chambon, C. Pinel, F. Rataboul, N. Essayem, Cellulose reactivity and glycosidic bond cleavage in aqueous phase by catalytic and non catalytic transformations, *Appl. Catal. A Gen.* 402 (2011) 1–10.
- [57] J.J. Wiesfeld, R. Gaquere, E.J.M. Hensen, Mesoporous doped tungsten oxide for glucose dehydration to 5-hydroxymethylfurfural, *ACS Sustain. Chem. Eng.* 7 (2019) 7552–7562.
- [58] Z. He, X. Ning, G. Yang, H. Wang, Y. Cao, F. Peng, H. Yu, Selective oxidation of glycerol over supported noble metal catalysts, *Catal. Today* 365 (2021) 162–171.
- [59] G. Miao, L. Shi, Z. Zhou, L. Zhu, Y. Zhang, X. Zhao, H. Luo, S. Li, L. Kong, Y. Sun, Catalyst design for selective hydrodeoxygenation of glycerol to 1, 3-propanediol, *ACS Catal.* 10 (2020) 15217–15226.
- [60] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. della Pina, From glycerol to value-added products, *Angew. Chem. Int. Ed.* 46 (2007) 4434–4440.
- [61] T. Jiang, M.X. Ren, S.S. Chen, Q. Huai, W.Y. Ying, F.H. Cao, Kinetics of hydrogenolysis of glycerol to ethylene glycol over Raney Ni catalyst, *Adv. Mat. Res. Trans. Tech. Publ.* (2014) 103–111.
- [62] S. Bagheri, N.M. Julkapli, W.A. Yehye, Catalytic conversion of biodiesel derived raw glycerol to value added products, *Renew. Sustain. Energy Rev.* 41 (2015) 113–127.
- [63] E. Nzediegwu, M.-J. Dumont, Chemo-catalytic transformation of cellulose and cellulose-derived waste materials into platform chemicals, *Waste Biomass-Valoriz.* 12 (2021) 2825–2851.
- [64] Y. Xiao, S. Xu, W. Zhang, J. Li, C. Hu, One-pot chemo-catalytic conversion of glucose to methyl lactate over In/γ-Al₂O₃ catalyst, *Catal. Today* 365 (2021) 249–256.
- [65] J. Pang, M. Zheng, X. Li, Y. Jiang, Y. Zhao, A. Wang, J. Wang, X. Wang, T. Zhang, Selective conversion of concentrated glucose to 1, 2-propylene glycol and ethylene glycol by using RuSn/AC catalysts, *Appl. Catal. B* 239 (2018) 300–308.
- [66] H. Li, S. Yang, A. Riisager, A. Pandey, R.S. Sangwan, S. Saravanamurugan, R. Luque, Zeolite and zeotype-catalysed transformations of biofuranic compounds, *Green. Chem.* 18 (2016) 5701–5735.
- [67] G. Li, E.A. Pidko, E.J.M. Hensen, A periodic DFT study of glucose to fructose isomerization on tungstite (WO₃·H₂O): influence of group IV–VI dopants and cooperativity with hydroxyl groups, *ACS Catal.* 6 (2016) 4162–4169.
- [68] G. Li, E.A. Pidko, E.J.M. Hensen, K. Nakajima, A. Density, Functional Theory Study of the Mechanism of Direct Glucose Dehydration to 5-Hydroxymethylfurfural on Anatase Titania, *ChemCatChem* 10 (2018) 4084–4089.
- [69] J. He, H. Li, S. Saravanamurugan, S. Yang, Catalytic upgrading of biomass-derived sugars with acidic nanoporous materials: structural role in carbon-chain length variation, *ChemSusChem* 12 (2019) 347–378.
- [70] X. Tong, Y. Ma, Y. Li, Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes, *Appl. Catal. A Gen.* 385 (2010) 1–13.
- [71] R. Ooms, M. Dusselier, J.A. Geboers, B.O. de Beeck, R. Verhaeven, E. Gobechiya, J.A. Martens, A. Redl, B.F. Sels, Conversion of sugars to ethylene glycol with nickel tungsten carbide in a fed-batch reactor: high productivity and reaction network elucidation, *Green. Chem.* 16 (2014) 695–707.
- [72] J. Guo, S. Zhu, Y. Cen, Z. Qin, J. Wang, W. Fan, Ordered mesoporous Nb–W oxides for the conversion of glucose to fructose, mannose and 5-hydroxymethylfurfural, *Appl. Catal. B* 200 (2017) 611–619, <https://doi.org/10.1016/j.apcatb.2016.07.051>.
- [73] M. Moliner, Y. Román-Leshkov, M.E. Davis, Tin-containing zeolites are highly active catalysts for the isomerization of glucose in water, *Proc. Natl. Acad. Sci.* 107 (2010) 6164–6168, <https://doi.org/10.1073/PNAS.1002358107>.
- [74] A.A. Marianou, C.M. Michailof, A. Pineda, E.F. Iliopoulou, K.S. Triantafyllidis, A. A. Lappas, Glucose to fructose isomerization in aqueous media over homogeneous and heterogeneous catalysts, *ChemCatChem* 8 (2016) 1100–1110, <https://doi.org/10.1002/CCTC.201501203>.
- [75] X. Zhou, M.W. Nolte, H.B. Mayes, B.H. Shanks, L.J. Broadbelt, Experimental and mechanistic modeling of fast pyrolysis of neat glucose-based carbohydrates. 1. Experiments and development of a detailed mechanistic model, *Ind. Eng. Chem. Res.* 53 (2014) 13274–13289.
- [76] V. Choudhary, S.H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N.S. Marinkovic, A. I. Frenkel, S.I. Sandler, D.G. Vlachos, Insights into the interplay of Lewis and Brønsted acid catalysts in glucose and fructose conversion to 5-(hydroxymethyl) furfural and levulinic acid in aqueous media, *J. Am. Chem. Soc.* 135 (2013) 3997–4006, https://doi.org/10.1021/JA3122763/SUPPL_FILE/JA3122763_SI_001.PDF.
- [77] M. Gu, Z. Shen, W. Zhang, M. Xia, J. Jiang, W. Dong, X. Zhou, Y. Zhang, Hydrogenolysis of Glucose into Propylene Glycol over Pt/SiO₂@ Mg (OH) 2 Catalyst, *ChemCatChem* 12 (2020) 3447–3452.
- [78] C. Liu, J.M. Carraher, J.L. Swedberg, C.R. Herndon, C.N. Fleitman, J.-P. Tessonnier, Selective base-catalyzed isomerization of glucose to fructose, *ACS Catal.* 4 (2014) 4295–4298.
- [79] L.-J. Liu, Z.-M. Wang, S. Fu, Z.-B. Si, Z. Huang, T.-H. Liu, H.-Q. Yang, C.-W. Hu, Catalytic mechanism for the isomerization of glucose into fructose over an aluminium-MCM-41 framework, *Catal. Sci. Technol.* 11 (2021) 1537–1543.
- [80] R. Insyani, A.F. Barus, R. Gunawan, J. Park, G.T. Jaya, H.S. Cahyadi, M.G. Sibi, S. K. Kwak, D. Verma, J. Kim, RuO₂-Ru/Hβ zeolite catalyst for high-yield direct conversion of xylose to tetrahydrofurfuryl alcohol, *Appl. Catal. B* 291 (2021), 120120, <https://doi.org/10.1016/j.apcatb.2021.120120>.
- [81] I. Jiménez-Morales, M. Moreno-Recio, J. Santamaría-González, P. Maireles-Torres, A. Jiménez-López, Production of 5-hydroxymethylfurfural from glucose using aluminium doped MCM-41 silica as acid catalyst, *Appl. Catal. B* 164 (2015) 70–76, <https://doi.org/10.1016/j.apcatb.2014.09.002>.
- [82] H.B. Mayes, M.W. Nolte, G.T. Beckham, B.H. Shanks, L.J. Broadbelt, The alpha-bet (a) of glucose pyrolysis: computational and experimental investigations of 5-hydroxymethylfurfural and levoglucosan formation reveal implications for cellulose pyrolysis, *ACS Sustain. Chem. Eng.* 2 (2014) 1461–1473.
- [83] C. Zhou, J. Zhao, H. Sun, Y. Song, X. Wan, H. Lin, Y. Yang, One-Step Approach to 2,5-Diformylfuran from Fructose over Molybdenum Oxides Supported on Carbon Spheres, *ACS Sustain. Chem. Eng.* 7 (2018) 315–323, <https://doi.org/10.1021/ACSUSCHEM.8B03470>.
- [84] N. Li, G.W. Huber, Aqueous-phase hydrodeoxygenation of sorbitol with Pt/SiO₂-Al₂O₃: Identification of reaction intermediates, *J. Catal.* 270 (2010) 48–59.
- [85] T.P. Vispute, G.W. Huber, Production of hydrogen, alkanes and polyols by aqueous phase processing of wood-derived pyrolysis oils, *Green. Chem.* 11 (2009) 1433–1445.
- [86] X. Wang, A.K. Beine, R. Palkovits, 1,2-propylene glycol and ethylene glycol production from lignocellulosic biomass, *Stud. Surf. Sci. Catal.* 178 (2019) 173–193, <https://doi.org/10.1016/B978-0-444-64127-4.00009-4>.
- [87] G. Zhao, M. Zheng, R. Sun, Z. Tai, J. Pang, A. Wang, X. Wang, T. Zhang, Ethylene glycol production from glucose over W-Ru catalysts: Maximizing yield by kinetic modeling and simulation, *AIChE J.* 63 (2017) 2072–2080, <https://doi.org/10.1002/AIC.15589>.
- [88] B. Kusserow, S. Schimpf, P. Claus, Hydrogenation of glucose to sorbitol over nickel and ruthenium catalysts, *Adv. Synth. Catal.* 345 (2003) 289–299, <https://doi.org/10.1002/ADSC.200390024>.
- [89] C.B. Schandel, M. Høj, C.M. Osmundsen, A.D. Jensen, E. Taarning, Thermal Cracking of Sugars for the Production of Glycolaldehyde and Other Small Oxygenates, *ChemSusChem* 13 (2020) 688–692.
- [90] L.-N. He, R.D. Rogers, D. Su, P. Tundo, Z. Conrad Zhang, Green Chemistry and Sustainable Technology Series editors, (n.d.). <http://www.springer.com/series/11661> (accessed December 9, 2021).
- [91] J. Zhang, B. Hou, A. Wang, Z. Li, H. Wang, T. Zhang, Kinetic study of the competitive hydrogenation of glycolaldehyde and glucose on Ru/C with or without AMT, *AIChE J.* 61 (2015) 224–238.
- [92] G. Zhao, M. Zheng, J. Zhang, A. Wang, T. Zhang, Catalytic conversion of concentrated glucose to ethylene glycol with semicontinuous reaction system, *Ind. Eng. Chem. Res.* 52 (2013) 9566–9572.
- [93] P. Kostetsky, L.J. Broadbelt, Progress in Modeling of Biomass Fast Pyrolysis: A Review, *Energy Fuels* 34 (2020) 15195–15216, <https://doi.org/10.1021/ACS.ENERGYFUELS.0C02295>.
- [94] C. Liu, Y. Shang, H. Qi, X. Wang, J. Gui, C. Zhang, Y. Zhu, Y. Li, Effect of the ZrO₂ phase on Pd-based bifunctional catalysts for the hydrogenolysis of glucose, *Catal. Commun.* 128 (2019), 105688.

- [95] C. Li, G. Xu, K. Li, C. Wang, Y. Zhang, Y. Fu, A weakly basic Co/CeO_x catalytic system for one-pot conversion of cellulose to diols: Kungfu on eggs, *Chem. Commun.* 55 (2019) 7663–7666.
- [96] H. Li, S. Saravanamurugan, S. Yang, A. Riisager, Direct transformation of carbohydrates to the biofuel 5-ethoxymethylfurfural by solid acid catalysts, *Green. Chem.* 18 (2016) 726–734.
- [97] F.H. Lv, R. Bi, Y.H. Liu, W.S. Li, X.P. Zhou, The synthesis of methyl lactate and other methyl oxygenates from cellulose, *Catal. Commun.* 49 (2014) 78–81, <https://doi.org/10.1016/j.catcom.2014.02.012>.
- [98] S. Yamaguchi, M. Yabushita, M. Kim, J. Hirayama, K. Motokura, A. Fukuoka, K. Nakajima, Catalytic Conversion of Biomass-Derived Carbohydrates to Methyl Lactate by Acid-Base Bifunctional γ -Al₂O₃, *ACS Sustain. Chem. Eng.* 6 (2018) 8113–8117, <https://doi.org/10.1021/ACSSUSCHEMENG.8B00809/ASSET/IMAGES/LARGE/SC-2018-00809J.0002.JPEG>.
- [99] Z. Liu, W. Li, C. Pan, P. Chen, H. Lou, X. Zheng, Conversion of biomass-derived carbohydrates to methyl lactate using solid base catalysts, *Catal. Commun.* 15 (2011) 82–87, <https://doi.org/10.1016/j.catcom.2011.08.019>.
- [100] D. Chu, Z. Luo, C. Zhao, Selective production of acetol or methyl lactate from cellulose over RuSn catalysts, *J. Energy Chem.* 73 (2022) 607–614, <https://doi.org/10.1016/j.jechem.2022.06.043>.
- [101] P. Bi, L. Wu, W. Hong, Nb/HUSY as a highly active catalyst for the direct transformation of fructose to methyl lactate, *Ceram. Int.* 46 (2020) 24045–24052, <https://doi.org/10.1016/j.ceramint.2020.06.182>.
- [102] D. Verma, R. Insyani, Y.W. Suh, S.M. Kim, S.K. Kim, J. Kim, Direct conversion of cellulose to high-yield methyl lactate over Ga-doped Zn/H-nanozeolite Y catalysts in supercritical methanol, *Green. Chem.* 19 (2017) 1969–1982, <https://doi.org/10.1039/C7GC00432J>.
- [103] B. Tang, S. Li, W.C. Song, E.C. Yang, X.J. Zhao, N. Guan, L. Li, Fabrication of Hierarchical Sn-Beta Zeolite as Efficient Catalyst for Conversion of Cellulosic Sugar to Methyl Lactate, *ACS Sustain. Chem. Eng.* 8 (2020) 3796–3808, https://doi.org/10.1021/ACSSUSCHEMENG.9B07061/ASSET/IMAGES/LARGE/SC9B07061_0013.JPEG.
- [104] L. Yang, X. Yang, E. Tian, V. Vattipalli, W. Fan, H. Lin, Mechanistic insights into the production of methyl lactate by catalytic conversion of carbohydrates on mesoporous Zr-SBA-15, *J. Catal.* 333 (2016) 207–216, <https://doi.org/10.1016/j.jcat.2015.10.013>.
- [105] M.A. Hossain, K.N. Mills, A.M. Molley, M.S. Rahaman, S. Tulaphol, S.B. Lalvani, J. Dong, M.K. Sunkara, N. Sathitsuksanoh, Catalytic isomerization of dihydroxyacetone to lactic acid by heat treated zeolites, *Appl. Catal. A Gen.* 611 (2021), 117979, <https://doi.org/10.1016/j.apcata.2020.117979>.
- [106] P. Wattanapaphawong, O. Sato, K. Sato, N. Mimura, P. Reubroycharoen, A. Yamaguchi, Conversion of Cellulose to Lactic Acid by Using ZrO₂-Al₂O₃ Catalysts, *Page 221*, 7, *Catalysts* 2017, Vol. 7 (2017) 221, <https://doi.org/10.3390/CATAL7070221>.
- [107] J. Duo, Z. Zhang, G. Yao, Z. Huo, F. Jin, Hydrothermal conversion of glucose into lactic acid with sodium silicate as a base catalyst, *Catal. Today* 263 (2016) 112–116, <https://doi.org/10.1016/j.cattod.2015.11.007>.
- [108] Z. Shen, W. Chen, W. Zhang, M. Gu, W. Dong, M. Xia, H. Si, Y. Zhang, Efficient Catalytic Conversion of Glucose into Lactic Acid over Y- β and Yb- β Zeolites, *ACS Omega* 7 (2022) 25200–25209, <https://doi.org/10.1021/ACSOMEGA.2C02051>.
- [109] M. Zheng, J. Pang, R. Sun, A. Wang, T. Zhang, Selectivity control for cellulose to diols: dancing on eggs, *ACS Catal.* 7 (2017) 1939–1954.
- [110] C.B. Schandel, M. Høj, C.M. Osmundsen, M.J. Beier, E. Taarning, A.D. Jensen, Kinetic Modeling of Gas Phase Sugar Cracking to Glycolaldehyde and Other Oxygenates, *ACS Sustain. Chem. Eng.* 9 (2021) 305–311, https://doi.org/10.1021/ACSSUSCHEMENG.0C07232/SUPPL_FILE/SC0C07232_SI_001.PDF.
- [111] P. Kostetskyy, M.W. Coile, J.M. Terrian, J.W. Collins, K.J. Martin, J.F. Brazdil, J. Broadbelt, Selective production of glycolaldehyde via hydrothermal pyrolysis of glucose: Experiments and microkinetic modeling, *J. Anal. Appl. Pyrolysis* 149 (2020), 104846.
- [112] A.H. Tullo, Haldor Topsoe, Braskem Investigate, Biobased ethylene glycol, *Chem. Eng. N.* 95 (2017) 10.
- [113] E. Forestier, C. Combeaud, N. Guigo, G. Corvec, C. Pradille, N. Sbirrazzuoli, N. Billon, Comparative Analysis of the Mechanical Behaviour of PEF and PET Uniaxial Stretching Based on the Time/Temperature Superposition Principle, *Page 3295*, 13, *Polymers* 2021 Vol. 13 (2021) 3295, <https://doi.org/10.3390/POLYM13193295>.
- [114] G. Li, E.A. Pidko, E.J.M. Hensen, A periodic DFT study of glucose to fructose isomerization on tungstite (WO₃-H₂O): influence of group IV–VI dopants and cooperativity with hydroxyl groups, *ACS Catal.* 6 (2016) 4162–4169.
- [115] E. Taarning, C. Osmundsen Mårup, X. Yang, B. Voss, S.I. Andersen, C.H. Christensen, E. Taarning, C.M. Osmundsen, X. Yang, B. Voss, S.I. Andersen, Zeolite-catalyzed Biomass Conversion to Fuels and Chemicals, *Pubs.Rsc.Org.*, 2017, <https://doi.org/10.1039/c004518g>.
- [116] A.D. Paulsen, M.S. Mettler, P.J. Dauenhauer, The role of sample dimension and temperature in cellulose pyrolysis, *Energy Fuels* 27 (2013) 2126–2134.
- [117] L. Chen, J. Zhao, S. Pradhan, B.E. Brinson, G.E. Scuseria, Z.C. Zhang, M.S. Wong, Ring-locking enables selective anhydrosugar synthesis from carbohydrate pyrolysis, *Green. Chem.* 18 (2016) 5438–5447.
- [118] E.M. Albuquerque, L.E.P. Borges, M.A. Fraga, Lactic acid production from aqueous-phase selective oxidation of hydroxyacetone, *J. Mol. Catal. A Chem.* 400 (2015) 64–70.
- [119] L. Zhang, Z. Bao, S. Xia, Q. Lu, K.B. Walters, Catalytic pyrolysis of biomass and polymer wastes, *Catalysts* Vol. 8 (2018) 659, <https://doi.org/10.3390/CATAL8120659>.
- [120] T. Kan, V. Strezov, T. Evans, J. He, R. Kumar, Q. Lu, Catalytic pyrolysis of lignocellulosic biomass: A review of variations in process factors and system structure, *Renew. Sustain. Energy Rev.* 134 (2020), 110305, <https://doi.org/10.1016/j.rser.2020.110305>.
- [121] K.B. Ansari, J.S. Arora, J.W. Chew, P.J. Dauenhauer, S.H. Mushrif, Fast pyrolysis of cellulose, hemicellulose, and lignin: effect of operating temperature on bio-oil yield and composition and insights into the intrinsic pyrolysis chemistry, *Ind. Eng. Chem. Res.* 58 (2019) 15838–15852.
- [122] J. Gupta, K. Papadakis, E.Y. Konyseva, Y. Lin, I. v Kozhevnikov, J. Li, CaO catalyst for multi-route conversion of oakwood biomass to value-added chemicals and fuel precursors in fast pyrolysis, *Appl. Catal. B* 285 (2021), 119858, <https://doi.org/10.1016/j.apcatb.2020.119858>.
- [123] R. Vinu, L.J. Broadbelt, A mechanistic model of fast pyrolysis of glucose-based carbohydrates to predict bio-oil composition, *Energy Environ. Sci.* 5 (2012) 9808–9826.
- [124] P.R. Patwardhan, D.L. Dalluge, B.H. Shanks, R.C. Brown, Distinguishing primary and secondary reactions of cellulose pyrolysis, *Bioresour. Technol.* 102 (2011) 5265–5269.
- [125] P.R. Patwardhan, J.A. Satrio, R.C. Brown, B.H. Shanks, Influence of inorganic salts on the primary pyrolysis products of cellulose, *Bioresour. Technol.* 101 (2010) 4646–4655.
- [126] P.R. Patwardhan, J.A. Satrio, R.C. Brown, B.H. Shanks, Product distribution from fast pyrolysis of glucose-based carbohydrates, *J. Anal. Appl. Pyrolysis* 86 (2009) 323–330.
- [127] C. Zhang, L. Chao, Z. Zhang, L. Zhang, Q. Li, H. Fan, S. Zhang, Q. Liu, Y. Qiao, Y. Tian, Pyrolysis of cellulose: Evolution of functionalities and structure of bio-char versus temperature, *Renew. Sustain. Energy Rev.* 135 (2021), 110416.
- [128] V. Seshadri, P.W.-T.J. of P. Chemistry, undefined 2012, Concerted reactions and mechanism of glucose pyrolysis and implications for cellulose kinetics, *ACS Publications*. 116, 2012: 11997–12013. <https://doi.org/10.1021/jp3085099>.
- [129] M.W. Easton, J.J. Nash, H.I. Kenttämä, Dehydration pathways for glucose and cellobiose during fast pyrolysis, *J. Phys. Chem. A* 122 (2018) 8071–8085.
- [130] X. Zhou, H.B. Mayes, L.J. Broadbelt, Fast pyrolysis of glucose-based carbohydrates with added NaCl Fast pyrolysis of glucose based carbohydrates with added NaCl part 1: Experiments and development of a mechanistic model, (n.d.).
- [131] M.S. Mettler, A.D. Paulsen, D.G. Vlachos, P.J. Dauenhauer, The chain length effect in pyrolysis: bridging the gap between glucose and cellulose, *Green. Chem.* 14 (2012) 1284–1288.
- [132] H.B. Mayes, M.W. Nolte, G.T. Beckham, B.H. Shanks, L.J. Broadbelt, The α -bet (a) of salty glucose pyrolysis: computational investigations reveal carbohydrate pyrolysis catalytic action by sodium ions, *ACS Catal.* 5 (2015) 192–202.
- [133] B. Hu, Q. Lu, X. Jiang, X. Dong, M. Cui, C. Dong, Y. Yang, Insight into the formation of Anhydrosugars in glucose pyrolysis: a joint computational and experimental investigation, *Energy Fuels* 31 (2017) 8291–8299.
- [134] P.A. Majerski, J.K. Piskorz, D.S.A.G. Radlein, Production of glycolaldehyde by hydrous thermolysis of sugars, 2006.
- [135] C.B. Schandel, Crack. Sugars Prod. Chem. (2020).
- [136] W. Faveere, T. Mihaylov, M. Pelckmans, K. Moonen, F. Gillis-D'Hamers, R. Bosschaerts, K. Pierloot, B.F. Sels, Glycolaldehyde as a bio-based C2 platform chemical: Catalytic reductive aminylation of vicinal hydroxyl aldehydes, *ACS Catal.* 10 (2019) 391–404.
- [137] D. Luo, W. Yin, D. Han, H. He, S. Xia, Glycolic acid and formic acid production from pyrolysis oil water-soluble fraction by catalytic oxidation, *Chem. Eng. Sci.* 239 (2021), 116644.
- [138] C.M. Osmundsen, S. Dahl, E. Taarning, J. Rossmeisl, Catalytic Conversion of Carbohydrates, *Catal. Convers. Carbohydr.*, Tech. Univ. Den. (2013).
- [139] W.J. Collins, J. Terrian, J. Brazdil, K. Martin, Processes for the pyrolysis of carbohydrates, WO2021231089A1, 2020, n.d.
- [140] A. Wang, T. Zhang, One-pot conversion of cellulose to ethylene glycol with multifunctional tungsten-based catalysts, *Acc. Chem. Res.* 46 (2013) 1377–1386, https://doi.org/10.1021/AR3002156/ASSET/IMAGES/LARGE/AR-2012-002156_0010.JPEG.
- [141] J. Zhang, B. Hou, A. Wang, Z. Li, H. Wang, T. Zhang, Kinetic study of retro-aldol condensation of glucose to glycolaldehyde with ammonium metatungstate as the catalyst, *AIChE J.* 60 (2014) 3804–3813.
- [142] E. Miliordos, S. Caratzoulas, D.G. Vlachos, A. periodic-DFT, study of retro-aldol fragmentation of fucose on MoO₃, *Appl. Catal. A Gen.* 530 (2017) 75–82.
- [143] Z. Xiao, S. Jin, G. Sha, C.T. Williams, C. Liang, Two-step conversion of biomass-derived glucose with high concentration over Cu–Cr catalysts, *Ind. Eng. Chem. Res.* 53 (2014) 8735–8743.
- [144] C. Liu, C. Zhang, S. Sun, K. Liu, S. Hao, J. Xu, Y. Zhu, Y. Li, Effect of WO_x on Bifunctional Pd–WO_x/Al₂O₃ Catalysts for the Selective Hydrogenolysis of Glucose to 1, 2-Propanediol, *ACS Catal.* 5 (2015) 4612–4623.
- [145] C.N. Satterfield, *Heterogeneous catalysis in practice*, McGraw-Hill Co. (1980).
- [146] N. Li, Y. Zheng, L. Wei, H. Teng, J. Zhou, Metal nanoparticles supported on WO₃ nanosheets for highly selective hydrogenolysis of cellulose to ethylene glycol, *Green. Chem.* 19 (2017) 682–691.
- [147] C. Luo, S. Wang, H. Liu, Cellulose conversion into polyols catalyzed by reversibly formed acids and supported ruthenium clusters in hot water, *Angew. Chem. Int. Ed.* 46 (2007) 7636–7639.
- [148] D. Chu, C. Zhao, Reduced oxygen-deficient CuWO₄ with Ni catalyzed selective hydrogenolysis of cellulose to ethylene glycol, *Catal. Today* 351 (2020), <https://doi.org/10.1016/j.cattod.2018.10.006>.

- [149] M. Lucas, K. Fabiřovicová, P. Claus, Hydrothermally Stable Ruthenium–Zirconium–Tungsten Catalyst for Cellulose Hydrogenolysis to Polyols, *ChemCatChem* 10 (2018) 612–618.
- [150] T. Kim, A. Burrows, C.J. Kiely, I.E. Wachs, Molecular/electronic structure–surface acidity relationships of model-supported tungsten oxide catalysts, *J. Catal.* 246 (2007) 370–381.
- [151] C. Liu, C. Zhang, S. Sun, K. Liu, S. Hao, J. Xu, Y. Zhu, Y. Li, Effect of WO_x on Bifunctional Pd–WO_x/Al₂O₃ Catalysts for the Selective Hydrogenolysis of Glucose to 1, 2-Propanediol, *ACS Catal.* 5 (2015) 4612–4623.
- [152] R.T. Sanderson, Principles of electronegativity part II. Applications, *J. Chem. Educ.* 65 (1988) 227.
- [153] T. Komanoya, K. Nakajima, M. Kitano, M. Hara, Synergistic catalysis by Lewis acid and base sites on ZrO₂ for Meerwein–Ponndorf–Verley reduction, *The, J. Phys. Chem. C* 119 (2015) 26540–26546.
- [154] J. Chai, S. Zhu, Y. Cen, J. Guo, J. Wang, W. Fan, Effect of tungsten surface density of WO₃–ZrO₂ on its catalytic performance in hydrogenolysis of cellulose to ethylene glycol, *RSC Adv.* 7 (2017) 8567–8574.
- [155] M. Zheng, A. Wang, N. Ji, J. Pang, X. Wang, T. Zhang, Transition metal–tungsten bimetallic catalysts for the conversion of cellulose into ethylene glycol, *ChemSusChem: Chem. Sustain. Energy Mater.* 3 (2010) 63–66.
- [156] N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J.G. Chen, Direct catalytic conversion of cellulose into ethylene glycol using nickel-promoted tungsten carbide catalysts, *Angew. Chem.* 120 (2008) 8638–8641.
- [157] Y. Zhang, A. Wang, T. Zhang, A new 3D mesoporous carbon replicated from commercial silica as a catalyst support for direct conversion of cellulose into ethylene glycol, *Chem. Commun.* 46 (2010) 862–864.
- [158] H. Wang, H. Xin, C. Cai, C. Zhu, Z. Xiu, Q. Liu, Y. Weng, C. Wang, X. Zhang, S. Liu, Selective C3–C4 Keto-Alcohol Production from Cellulose Hydrogenolysis over Ni–WO_x/C Catalysts, *ACS Catal.* 10 (2020) 10646–10660.
- [159] Y. Cao, J. Wang, M. Kang, Y. Zhu, Catalytic conversion of glucose and cellobiose to ethylene glycol over Ni–WO₃/SBA-15 catalysts, *RSC Adv.* 5 (2015) 90904–90912.
- [160] Y. Cao, J. Wang, M. Kang, Y. Zhu, Efficient synthesis of ethylene glycol from cellulose over Ni–WO₃/SBA-15 catalysts, *J. Mol. Catal. A Chem.* 381 (2014) 46–53.
- [161] K. Zhang, G. Yang, G. Lyu, Z. Jia, L.A. Lucia, J. Chen, One-pot solvothermal synthesis of graphene nanocomposites for catalytic conversion of cellulose to ethylene glycol, *ACS Sustain. Chem. Eng.* 7 (2019) 11110–11117.
- [162] Y. Liu, Y. Liu, Y. Zhang, The synergistic effects of Ru and WOX for aqueous-phase hydrogenation of glucose to lower diols, *Appl. Catal. B* 242 (2019) 100–108.
- [163] Z. Xiao, Q. Zhang, T. Chen, X. Wang, Y. Fan, Q. Ge, R. Zhai, R. Sun, J. Ji, J. Mao, Heterobimetallic catalysis for lignocellulose to ethylene glycol on nickel–tungsten catalysts: influenced by hydroxy groups, *Fuel* 230 (2018) 332–343.
- [164] M. Gu, Z. Shen, L. Yang, W. Dong, L. Kong, W. Zhang, B.-Y. Peng, Y. Zhang, Reaction route selection for cellulose hydrogenolysis into C₂/C₃ Glycols by ZnO-modified Ni–W/β-zeolite catalysts, *Sci. Rep.* 9 (2019) 1–10.
- [165] Z. Xiao, X. Wang, Q. Yang, C. Xing, Q. Ge, X. Gai, J. Mao, J. Ji, Fabrication of immobilized nickel nanoclusters decorated by CxNy species for cellulose conversion to C₂, 3 oxygenated compounds: Rational design via typical C- and N-sources, *J. Energy Chem.* 50 (2020) 25–36.
- [166] S. Sreekantan, A.A. Kirali, B. Marimuthu, Enhanced one-pot selective conversion of cellulose to ethylene glycol over NaZSM-5 supported metal catalysts, *N. J. Chem.* (2021).
- [167] J. Yu, J. Liang, X. Chen, L. Wang, X. Wei, Y. Li, Y. Qin, Synergistic Effect of Ni/W/Cu on MgAl₂O₄ for One-Pot Hydrogenolysis of Cellulose to Ethylene Glycol at a Low H₂ Pressure, *ACS Omega* 6 (2021) 11650–11659.
- [168] M.S. Hamdy, M.A. Eissa, S.M.A.S. Keshk, New catalyst with multiple active sites for selective hydrogenolysis of cellulose to ethylene glycol, *Green. Chem.* 19 (2017) 5144–5151.
- [169] N. Li, X. Liu, J. Zhou, Q. Ma, M. Liu, W. Chen, Enhanced Ni/W/Ti Catalyst Stability from Ti–O–W Linkage for Effective Conversion of Cellulose into Ethylene Glycol, *ACS Sustain. Chem. Eng.* 8 (2020), <https://doi.org/10.1021/acsschemeng.0c00836>.
- [170] Q. Xin, L. Jiang, S. Yu, S. Liu, D. Yin, L. Li, C. Xie, Q. Wu, H. Yu, Y. Liu, Bimetal oxide catalysts selectively catalyze cellulose to ethylene glycol, *J. Phys. Chem. C* 125 (2021) 18170–18179.
- [171] Q. Xin, S. Yu, L. Jiang, D. Yin, L. Li, C. Xie, Q. Wu, H. Yu, Y. Liu, Y. Liu, Bifunctional catalyst with a yolk–shell structure catalyzes glucose to produce ethylene glycol, *J. Phys. Chem. C* 125 (2021) 6632–6642.
- [172] M. Lv, Q. Xin, D. Yin, Z. Jia, C. Yu, T. Wang, S. Yu, S. Liu, L. Li, Y. Liu, Magnetically recoverable bifunctional catalysts for the conversion of cellulose to 1,2-propylene glycol, *ACS Sustain. Chem. Eng.* 8 (2020) 3617–3625, https://doi.org/10.1021/ACSSUSCHEMENG.9B06264/SUPPL_FILE/SC9B06264_SI_001.PDF.
- [173] W. Liu, Y. Chen, H. Qi, L. Zhang, W. Yan, X. Liu, X. Yang, S. Miao, W. Wang, C. Liu, A. Wang, J. Li, T. Zhang, A Durable Nickel Single-Atom Catalyst for Hydrogenation Reactions and Cellulose Valorization under Harsh Conditions, *Angew. Chem.* 130 (2018) 7189–7193, <https://doi.org/10.1002/ANGE.201802231>.
- [174] H. Xin, H. Wang, S. Li, X. Hu, C. Wang, L. Ma, Q. Liu, Efficient production of ethylene glycol from cellulose over Co@C catalysts combined with tungstic acid, *Sustain. Energy Fuels* 6 (2022) 2602–2612, <https://doi.org/10.1039/D2SE00386D>.
- [175] J. Pang, M. Zheng, X. Li, J. Sebastian, Y. Jiang, Y. Zhao, A. Wang, T. Zhang, Unlock the compact structure of lignocellulosic biomass by mild ball milling for ethylene glycol production, *ACS Sustain. Chem. Eng.* 7 (2019) 679–687, https://doi.org/10.1021/ACSSUSCHEMENG.8B04262/ASSET/IMAGES/LARGE/SC-2018-04262K_0009.JPEG.
- [176] S.T. Oyama, Introduction to the chemistry of transition metal carbides and nitrides, in: *The Chemistry of Transition Metal Carbides and Nitrides*, Springer, 1996, pp. 1–27.
- [177] M.M. Sullivan, A. Bhan, Acetone Hydrodeoxygenation over Bifunctional Metallic–Acidic Molybdenum Carbide Catalysts, *ACS Catal.* 6 (2016) 1145–1152, https://doi.org/10.1021/ACSCATAL.5B02656/SUPPL_FILE/CS5B02656_SI_001.PDF.
- [178] T. Xiao, H. Wang, A.P.E. York, V.C. Williams, M.L.H. Green, Preparation of nickel–tungsten bimetallic carbide catalysts, *J. Catal.* 209 (2002) 318–330.
- [179] L.S. Ribeiro, J.J. de Melo Órfão, M.F.R. Pereira, Direct catalytic conversion of agro-forestry biomass wastes into ethylene glycol over CNT supported Ru and W catalysts, *Ind. Crops Prod.* 166 (2021), 113461.
- [180] T.D.J. te Molder, S.R.A. Kersten, J. Lange, M.P. Ruiz, Cellulosic glycols: an integrated process concept for lignocellulose pretreatment and hydrogenolysis, *Biofuels*. Bioproducts and Biorefining, 2021.
- [181] T.D.J. te Molder, S.R.A. Kersten, J.P. Lange, M.P. Ruiz, Ethylene Glycol from Lignocellulosic Biomass: Impact of Lignin on Catalytic Hydrogenolysis, in: *Ind Eng Chem Res*, 60, 2021, pp. 7043–7049.
- [182] C. Suresh, D. Santharaj, M. Gurulakshmi, G. Deepa, M. Selvaraj, N.R. Sasi Rekha, K. Shanthi, Mo–Ni/Al–SBA-15 (sulfide) catalysts for hydrodenitrogenation: effect of Si/Al ratio on catalytic activity, *ACS Catal.* 2 (2012) 127–134.
- [183] H. Wang, H. Xin, C. Cai, C. Zhu, Z. Xiu, Q. Liu, Y. Weng, C. Wang, X. Zhang, S. Liu, Selective C3–C4 Keto-Alcohol Production from Cellulose Hydrogenolysis over Ni–WO_x/C Catalysts, *ACS Catal.* 10 (2020) 10646–10660.
- [184] J. Liu, H. Qi, H. Ren, I. Prakash, Y. Shi, Method for preparing diol, EP3653 595 A1, 2015.
- [185] Y. Liu, Y. Liu, Q. Wu, Y. Zhang, Catalytic conversion of glucose into lower diols over highly dispersed SiO₂-supported Ru–W, *Catal. Commun.* 129 (2019), <https://doi.org/10.1016/j.catcom.2019.105731>.
- [186] J. Zhang, X. Yang, B. Hou, A. Wang, Z. Li, H. Wang, T. Zhang, Comparison of cellobiose and glucose transformation to ethylene glycol, *Chin. J. Catal.* 35 (2014) 1811–1817.
- [187] Z. Xiao, J. Mao, C. Jiang, C. Xing, J. Ji, Y. Cheng, One-pot selective conversion of cellulose into low carbon polyols on nano-Sn based catalysts, *J. Renew. Sustain. Energy* 9 (2017), 024703.
- [188] R. Sun, M. Zheng, J. Pang, X. Liu, J. Wang, X. Pan, A. Wang, X. Wang, T. Zhang, Selectivity-Switchable Conversion of Cellulose to Glycols over Ni–Sn Catalysts, *ACS Catal.* 6 (2016), <https://doi.org/10.1021/acscatal.5b01807>.
- [189] Z. Tan, L. Shi, Y. Zan, G. Miao, S. Li, L. Kong, S. Li, Y. Sun, Crucial role of support in glucose selective conversion into 1, 2-propanediol and ethylene glycol over Ni-based catalysts: A combined experimental and computational study, *Appl. Catal. A Gen.* 560 (2018) 28–36.
- [190] P. Yazdani, B. Wang, Y. Du, S. Kawi, A. Borgna, Lanthanum oxycarbonate modified Cu/Al₂O₃ catalysts for selective hydrogenolysis of glucose to propylene glycol: base site requirements, *Catal. Sci. Technol.* 7 (2017) 4680–4690.
- [191] T.T. Gao, Y.G. Sun, Y.B. Zhu, F. Lin, Y.D. Zhong, Y.Y. Li, W.X. Ji, Y.L. Ma, Ni-Based multifunctional catalysts derived from layered double hydroxides for the catalytic conversion of cellulose to polyols, *N. J. Chem.* 46 (2022) 16058–16067, <https://doi.org/10.1039/D2NJ02104H>.
- [192] Z. Xiao, S. Jin, M. Pang, C. Liang, Conversion of highly concentrated cellulose to 1, 2-propanediol and ethylene glycol over highly efficient CuCr catalysts, *Green. Chem.* 15 (2013) 891–895.
- [193] A.A. Kirali, S. Sreekantan, B. Marimuthu, Fabrication of mesoporous carbon supported Ni–Mo catalysts for the enhanced conversion of glucose to ethylene glycol, *N. J. Chem.* 44 (2020) 15958–15965.
- [194] S. Sreekantan, A.A. Balachandran Kirali, B. Marimuthu, Catalytic conversion of sucrose to 1,2-propanediol over alumina-supported Ni–Mo bimetallic catalysts, *Sustain. Energy Fuels* 6 (2022) 3681–3689, <https://doi.org/10.1039/D2SE00610C>.
- [195] J. Clayden, N. Greeves, S. Warren, P. Wothers, *Org. Chem.* (2001).
- [196] D.K. Sohounloue, C. Montassier, J. Barbier, Catalytic hydrogenolysis of sorbitol, *React. Kinet. Catal. Lett.* 22 (1983) 391–397.
- [197] P. Yazdani, B. Wang, F. Gao, S. Kawi, A. Borgna, Role of the strong Lewis base sites on glucose hydrogenolysis, *ChemCatChem* 10 (2018) 3845–3853.